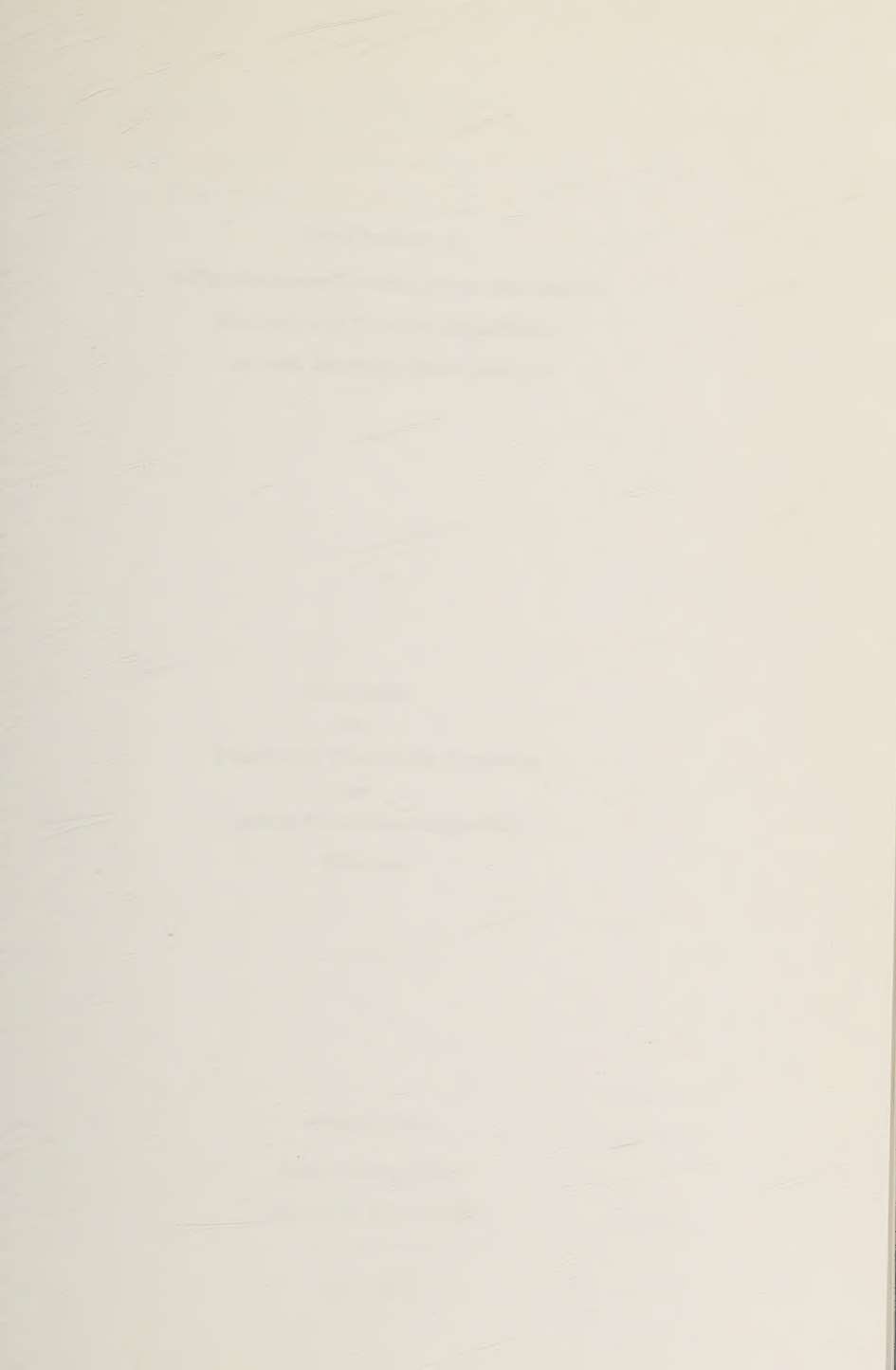


The Chemistry of
9-Fluorenylidene-Tetramethylpiperidino-Borane:
Reactions with Covalent Metal Halides
and with Transition Metal Carbonyls

Disbui. München
1988

Scott Whitney Helm





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The Chemistry of
9-Fluorenylidene-Tetramethylpiperidino-Borane:
Reactions with Covalent Metal Halides
and with Transition Metal Carbonyls

Dissertation
der
Fakultät für Chemie und Pharmazie
der
Ludwig-Maximilians-Universität
München

vorgelegt von
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aus Akron, Ohio (USA)

Juli 1988

1. Berichterstatter: Prof. Dr. H. Nöth

2. Berichterstatter: Prof. Dr. W. Beck

Tag der mündlichen Prüfung: der 25. Juli 1988

The following work was carried out between October 1, 1985 and July 4, 1988
in the Institut für Anorganische Chemie der Universität München under the
direction and tutelage of

Prof. Dr. H. Nöth.

"I have measured out my life in spoonfuls of coffee."

-T. S. Eliot in

"The Lovesong of J. Alfred Prufrock"

For my parents:

You never said no.

Acknowledgments

I would like to take this opportunity to thank all persons who have in any way contributed to the success of this work.

I would first like to express my gratitude to my teacher Prof. Dr. H. Nöth for acceptance into his research group and for assistance and guidance with the many problems associated with study in a foreign country. I would furthermore like to thank him for his encouragement, interest and helpfulness throughout the course of this work.

In addition, I would like to express my most sincere thanks to the following people:

- all members of the Nöth research groups for stimulating and extremely helpful discussions. In particular I would like to thank Dr. B. Brellochs for his help and encouragement in getting Chapter 5 off the ground. Discussions with Mr. G. Linti were also extremely helpful. I would also like to thank Prof. Dr. W. Beck for helpful discussions and friendly encouragement with the transition metal chemistry. I am indebted to him and his group for a good deal of the chemistry I have learned in Munich. From the Beck research group, cooperative work was carried out with Ms. E. Fritsch and Dr. P. Fritz for which I would like to thank them both.
- Ms. D. Bleif for typing this manuscript. Without her, I *never* would have made it.
- Mr. E. Striedl for assistance with the Chemtext program.
- Mr. S. Böck, Mr. D. Loderer, Mr. G. Linti, Prof. Dr. H. Nöth and Dr. W. Rattay for the X-ray structural determinations.
- all of my colleagues who sacrificed their own time for NMR measurements, in particular: Mr. S. Böck, Dr. B. Brellochs, Mr. G.

Geisberger, Mr. V. Hyna, Mr. E. Mayer, Ms. P. Seiberlich, Ms. B. Stöber, and the Drs. A. and U. Wietelmann (Wietelmänner?).

- Dr. K. Karaghiosoff for ^{13}C -NMR measurements.
- Mr. P. Rahm for low-temperature NMR measurements.
- Ms. U. Starra for fantastic routine NMR measurements.
- Mr. A. Gupta and Mr. J. Stehlin for enthusiastic assistance in the course of their "F-Praktika."
- Ms. P. Lenke for technical assistance while her real boss was on vacation.
- Ms. B. Hubert for the same.
- the members of the analytical and spectroscopic departments for the reliable analyses and measurements.
- Mr. H. Lenke and Mr. R. Klinger for technical assistance with the glass apparatus.
- Dr. Aidan Kendrick for reading the entire manuscript in one evening without dosing off.
- And last but certainly not least I would like to thank my friends Sigi Dresler and Aidan Kendrick for moral support and a whole lot of fun throughout the course of this work and my stay in Germany.
- I close with a note of thanks to the German Academic Exchange Service whose financial support made my efforts here possible in the first two years (1985-1987).

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Abbreviations used in this work:

R, R'	:	alkyl, aryl
X, Y	:	functional group
Me	:	methyl
Et	:	ethyl
Pr	:	propyl
iPr	:	isopropyl
Bu	:	butyl
tBu	:	tert. butyl
Ph	:	phenyl
tmp	:	2,2,6,6-tetramethylpiperidino
Cp	:	cyclopentadienyl
Cp'	:	(methyl)cyclopentadienyl
C ₁₃ H ₈	:	fluorenylidene
C ₁₃ H ₉	:	fluorenyl
RT	:	room temperature
S.M.	:	starting material
h	:	hours
min	:	minutes
s	:	singlet
d	:	doublet or days, according to context
t	:	triplet
q	:	quartet
quin	:	quintet
m	:	multiplet
I.R.	:	infrared spectrum
NMR	:	nuclear magnetic resonance spectrum
MS	:	mass spectrum
b.p.	:	boiling point
m.p.	:	melting point
dec.	:	decomposition

Introduction

In the last 10 years main-group chemistry has entered a renaissance. Whereas many researchers were prepared to accept the notion that element-carbon and element-nitrogen multiple bond systems were not capable of existence, others worked on the development of new synthetic principles which would pave the way for the existence of these "non-existent" compounds. One of the most powerful of these synthetic principles has been that of kinetic stabilization of metastable structural elements *via* the introduction of bulky substituents such as CMe_3 , super-mesityl, $\text{C}(\text{SiMe}_3)_3$, or tmp (2,2,6,6-tetramethylpiperidino). In the case of the element boron, such kinetic stabilization has often been supplemented by electronic stabilization through the use of bulky amine substituents, whose lone pairs can be used to "saturate" the boron atom electronically *via* B-N ($\text{p}\pi\text{-p}\pi$) interaction. This methodology has resulted in the syntheses of $\text{B}=\text{C}^{(1),(2)}$ and $\text{B}\equiv\text{N}^{(3),(4)}$ multiple-bond systems, all as stable isolable substances.

Because these compounds are kinetically stabilized species, they have proven to possess high reactivities and are useful starting materials in the syntheses of variously substituted boranes. Work with the amino-imino-borane has resulted in the syntheses of a large series of N-substituted bis(amino)boranes.⁽⁵⁾

At the start of this work several examples of the addition of boron halides and two examples of the addition of an (alkyl)phosphous dihalide across the $\text{B}=\text{C}$ double bond to the corresponding C-functionalized (amino)(halogeno)(organyl) boranes were known^{(6),(7)}. In addition, Glaser had studied the addition reaction of compounds of the type HX , as well as a series of (2+2) cycloadditions to the corresponding oxaboretanes⁽⁶⁾. E. Mayer expanded on the cycloaddition work to include thioketones and acetamides⁽⁸⁾.

The goal of the present work is to extend the study of the reactivity of the system (9-fluorenylidene)(2,2,6,6-tetramethylpiperidino)borane (Fig. I.1, from this point on to be abbreviated as $\text{tmpB}=\text{CR}_2$) to include metal halides of Main Groups IV and V. In particular, substituent effects (both steric and electronic) on the

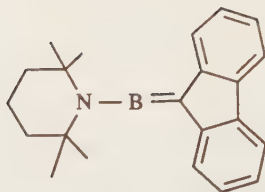


Fig I.1: amino-fluorenylidene-borane

reaction paths should be explored and similarities between the reactivity of $\text{tmpB}=\text{CR}_2$ and other "electron-deficient" alkenes (eg. C_2F_2) should be investigated. Just as $\text{tmpB}\equiv\text{N}^t\text{Bu}$ has proven to be a powerful synthon for many N-functionalized boranes⁵), the potential of $\text{tmpB}=\text{CR}_2$ as a building block for stable C-functionalized boranes should also be explored. The reactivity of the Main Group V compounds towards $\text{tmpB}=\text{CR}_2$ is presented in Chapters 1 (acyclic compounds) and 2 (cyclic compounds). The chemistry with the halides of Main Group IV is presented in Chapter 3.

Another aspect of the present work is to explore the potential of $\text{tmpB}=\text{CR}_2$ as a transition metal complex ligand. The fluorenyl ligand was chosen by Glaser for the synthesis of the first "true" $\text{B}=\text{C}$ double bond system because of its steric bulk and its mesomeric stabilizing effect. That the system is indeed mesomerically stabilized is evidenced by its slightly longer $\text{B}=\text{C}$ bond length than in the recently synthesized system, $(^i\text{Pr}_2\text{N})\text{B}=\text{C}(\text{SiMe}_3)_2$ for which no similar mesomeric effect can play a role²). However, the choice of the fluorenyl ligand should also expand the coordination possibilities available to the system. The unsubstituted fluorenyl ligand was known to possess an interesting and varied chemistry as a complex ligand. However, its chemistry is also noticeably less vast than that of other cyclopentadienyl analogues⁹). The effect of (amino)boryl substitution on the tendency of the fluorenyl ligand to coordinate in a η^3 - or η^5 -manner should be investigated (Chapter 3). A review of the chemistry of the unsubstituted fluorenyl ligand is also presented in order to place the present work in historical perspective (Introduction to Chapter 3).

(2+2) cycloadditions are among the most important reactions of the

$\text{tmpB}=\text{CR}_2$ system. Their general utility in the syntheses of various inorganic heterocycles has been demonstrated by Glaser and Mayer^(6),8). A goal of the present work is to extend these investigations to include variously substituted ketones, esters, thioesters, acid chlorides, and amino acids. Reactions involving (2+2) cycloadditions at ligands attached to transition metals should also be explored (Chapter 4).

Finally, the reactivity of $\text{tmp}=\text{CR}_2$ in ligand substitution reactions at transition metals to yield novel bora-olefin complexes should be explored. There is only a limited number of paths which lead to the formation of boron-transition metal bonds¹⁰⁾. Attempts to coordinate the $\text{B}\equiv\text{N}$ triple bond in a "side-on" η^2 -fashion have only resulted in coordination *via* the imino-nitrogen lone pair^{5a),11)}. No metal-boron bonds have resulted from such reactions. The bora-olefin $\text{tmpB}=\text{CR}_2$ should, however, prove to be a much poorer donor and, therefore, behave more like a "normal" asymmetric olefin (Chapter 5). A review of previously known transition metal-boron bond forming reactions is also presented (Introduction, Chapter 5).

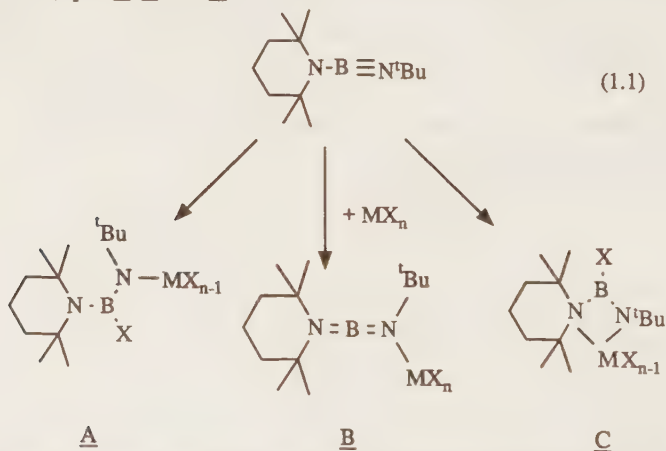
Chapter 1:

Reaction of 9-Fluorenylidene-2,2,6,6-tetramethylpiperidino-borane with Acyclic Compounds of Phosphorous(III), Arsenic(III), and Antimony(III)

1.1 Introduction

Since the successful synthesis of amino-imino-boranes¹⁾, a large number of N-functionalized bis(amino)-boron halides have become accessible *via* insertion reactions of element halides into the boron-nitrogen triple bond²⁾⁻⁵⁾.

For the products of such reactions, three possible structural types have been ascertained (eq. 1, A, B, and C):



With element-halides of main group III, one obtains either the Lewis acid-base adducts of type B or the intramolecularly cyclized diborylamines, C^{1),2)}. Reaction of $\text{tmpB} \equiv \text{N}^t\text{Bu}$ with compounds of the type ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$; $\text{X} = \text{Hal}$; $\text{R} = \text{Me}$) results in the formation of the acyclic adducts, A^{3),4)}. Similar systematic investigation of the reactivity of $\text{tmpB} \equiv \text{N}^t\text{Bu}$ with phosphorous, arsenic and antimony trihalides produced acyclic insertion products, A. However, Lewis acid-base adducts are formed (type B) in the case of the iodides.

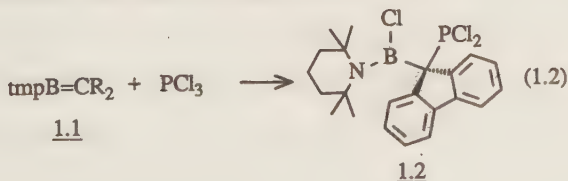
We investigated the reactions between $\text{tmpB} = \text{CR}_2$ and compounds of the type $\text{ER}_n\text{X}_{3-n}$ ($\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$; $\text{R} = \text{alkyl}, \text{aryl}, \text{NMe}_2, \text{OMe}$) in the hope of

uncovering similar reactivity patterns. Moreover, the products, C-functionalized (amino)(organyl)boron halides, could prove to be useful synthons, and they are furthermore not readily accessible by other synthetic routes.

1.2 Reaction of tmp=CR₂ with Acyclic Phosphorous(III)-Compounds

1.2.1 Reaction with Phosphorous Trihalides

Equimolar addition of PCl₃ to a solution of tmpB=CR₂, 1.1, in toluene results in the mono-insertion product 1.2 (as in eq. 1.2).



1.2 can be isolated in good yield as a fairly stable crystalline product from a hexane/toluene mixture at low temperature. The compound is extremely air- and moisture-sensitive, reacting readily with excess H₂O and MeOH in exothermic reactions to undefined products. If stored under an atmosphere of dry nitrogen at room temperature, the product is stable. It was fully characterized by analysis, NMR, I.R. and mass spectroscopy. NMR data are listed in Tables 1-3. A numbering scheme for the fluorenyl region of the ¹³C-NMR spectra is given in Fig. 1.1. All discussions of ¹³C-NMR data in this work rely on the numbering scheme found in Fig. 1.1 (page 11).

The mass spectrum of 1.2 contains the parent ion peak at m/e = 452 (¹¹B, ³⁵Cl), for which the calculated and experimental isotope patterns are in good agreement. The mass spectrum further contains the (M-PCl₂)⁺ fragment as the base peak (m/e = 350, ¹¹B, ³⁵Cl).

The suggested structure for 1.2 is further supported by the ^{11}B -NMR spectrum: the ^{11}B -resonance at 42.6 ppm is within the region expected for a chloro(organyl)(tmp)borane. (For comparison, the HCl adduct of 1.1, tmp-B(Cl)(C₁₃H₉) exhibits a ^{11}B -resonance of $\delta^{11}\text{B} = 42.3 \text{ ppm}^{(6)}$). When compared with the MePCl₂ adduct of 1.1⁽⁶⁾, $\delta^{11}\text{B} = 44.8 \text{ ppm}$ the ^{11}B -resonance of 1.2 is found to be shifted 2.5 ppm to higher field. The reason for this most likely lies in the greater steric requirements of the MePCl- *versus* the PCl₂-unit, which results in the tmp ring being twisted in such a way as to decrease p π -p π overlap between B and N⁽⁹⁾.

The ^{31}P -chemical shift of 190 ppm is in good agreement with (alkyl)dichlorophosphanes, lying between values found for MePCl₂ ($\delta^{31}\text{P} = 192 \text{ ppm}$) and (benzyl)PCl₂ ($\delta^{31}\text{P} = 180 \text{ ppm}$)^(7,8).

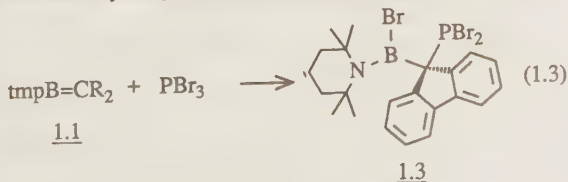
In the ^1H -NMR spectrum, the tmp methyl groups are significantly shielded ($\delta^1\text{H} = 0.90 \text{ ppm}$) as a result of the anisotropic effect of the neighbouring fluorene group. That only one signal is found for the two sets of tmp methyl groups indicates equivalence on the NMR time scale and, hence, free rotation about the B-N bond. Similarly, the tmp methyl groups in the MePCl₂ adduct of 1.1 were found at 0.98 ppm⁽⁶⁾. Otherwise, the methylene protons from tmp at $\delta^1\text{H} = 1.40\text{-}1.44 \text{ ppm}$ and the fluorene protons at $\delta^1\text{H} = 7.18\text{-}7.43$ and $7.69\text{-}7.90 \text{ ppm}$ present no unexpected details.

For the MePCl₂ addition product, an interpretation of the signals in the fluorene region of the ^{13}C -NMR spectrum could not be undertaken because the chirality of the phosphorous atom, together with the coupling between ^{31}P and ^{13}C , resulted in an extremely complex spectrum⁽⁶⁾. In the case of the compound 1.2, the molecule is more symmetrical, and assignments of individual ^{13}C -NMR signals to the fluorene C-atoms is possible. These assignments are given in Table 3b. $J(^{31}\text{P}\text{-}^{13}\text{C})$ coupling constants are also found and lie in the range of 1.5 to 8.1 Hz. The rather large $^3J(^{31}\text{P}\text{-}^{13}\text{C})$ coupling of 7.3 Hz for C11 is nonetheless within the range of other 3J -coupling constants. For example, in (n-Bu)₃P, $^1J(^{31}\text{P}\text{-}^{13}\text{C})$ is 0.9 Hz whereas 3J is larger with a value of 12.5 Hz⁽¹⁰⁾ (these coupling constants are, however, opposite in sign). It is furthermore worthy of note that Glaser⁽⁶⁾ could not

always unambiguously assign ^{13}C -NMR signals to the three "benzene-like" C-atoms, C11, C12 and C13, in the various addition products he synthesized. The magnitude of the ^{31}P - ^{13}C coupling in 1.2, however, rules out the possibility that the C-atom involved is C12 or C13, as this would imply a 4J or $^5J(^{31}\text{P}$ - $^{13}\text{C})$ value larger than 2J and 3J , a phenomenon not often, if ever, encountered^(10,7). Thus the assignment of the 7.3 Hz coupling constant is made to C11.

An additional clarification provided by the symmetrical (and, hence, spectroscopically less complex) nature of 1.2 is an approximate assignment of ^{13}C -NMR shifts in the product formed by the reaction of 1.1 and $^i\text{PrPCl}_2$ ⁽¹¹⁾. As with the MePCl_2 adduct, the addition product of $^i\text{PrPCl}_2$ contains a chiral phosphorous atom, thereby resulting in the loss of the plane of symmetry perpendicular to the fluorenyl plane. The authors reported $^4J(^{31}\text{P}$ - $^{13}\text{C})$ for C14 to be 7.2 Hz. Based on the ^{13}C -NMR spectrum of 1.2, this is highly unlikely. What is more likely is that two different signals are found for C14 and C14', which, because of the chirality at phosphorous, are no longer equivalent. The $^4J(^{31}\text{P}$ - $^{13}\text{C})$ value is probably so small as not to be observed. In a similar fashion, the reported 3J coupling to C15 of 34.1 Hz is far too large when compared with values found for 1.2 or other similar (alkyl)phosphorous dihalides⁽¹⁰⁾. Again, the 34.1 Hz "coupling constant" was most likely the result of the loss of symmetry and hence the division of the fluorene signals into two sets of six. As will be seen later, this result is supported by many different examples throughout this work, examples involving both chiral and achiral phosphorous centers containing various substituents (see other sections of this chapter and Chapter 2).

Like PCl_3 , PBr_3 reacts with $\text{tmpB}=\text{CR}_2$ at room temperature in an exothermic reaction to yield 1.3, according to equation 1.3.



The reaction is complete after 12h as detected by ^{11}B - and ^{31}P -NMR.

Using a slight excess of PBr_3 does not result in a decreased yield or undesired side reactions. (By ^{11}B -NMR, the product was stable in the presence of an excess of PBr_3 for 1d at room temperature.) Work-up by removal of all volatiles followed by crystallization from a hexane:toluene mixture yields a colorless, air- and moisture-sensitive powder, which can be stored for long periods at room temperature under N_2 . The product 1.3 was characterized by analysis, NMR, I.R. and mass spectroscopy.

The parent ion expected at $m/e = 583$ is found at neither 70 nor 15 eV. The peak with the highest m/e is also the base peak at $m/e = 394$ (^{11}B , ^{79}Br , $(\text{M-PBr}_2)^+$). Another peak of high intensity (ca. 60%) is assigned to the cation $(\text{tmpB}=\text{CR}_2)^+$ at $m/e = 315$. The fragment $(\text{PBr}_2)^+$ is also found with high intensity (50%).

The suggested structure of 1.3 is supported by the NMR data obtained. The ^{11}B -chemical shift of 43.0 ppm corresponds to a bromo(organyl)(tmp)borane. The compound analogous to 1.3 which contains a proton at C9 instead of a PBr_2 -unit is known and its ^{11}B -NMR signal at 41.7 ppm agrees well with that found for 1.3⁶.

The ^{31}P -chemical shift also points to the formation of 1.3. The ^{31}P -NMR signal for PBr_3 at 229 ppm is ca. 29 ppm downfield from the ^{31}P -NMR shift of 1.3 ($\delta^{31}\text{P} = 200$ ppm). This correlates well with the result for 1.2 for which $\Delta\delta^{31}\text{P}$ between starting material (PCl_3) and addition product is 30 ppm.

As in 1.2 the tmp methyl protons in the ^1H -NMR spectrum of 1.3 are found at relatively high field as a result of the anisotropic effect of the fluorenyl group ($\delta^1\text{H} = 0.95$ ppm). One signal is found for the four methyl groups, indicating free rotation about the B-N bond. The signals for the methylene protons in tmp as well as the fluorene protons show no unusual features.

The ^{13}C -NMR spectrum of 1.3 indicates a symmetric environment about the fluorenyl group as in 1.2, and the fluorene signals and ^{31}P - ^{13}C coupling constants of 1.2 and 1.3 correlate extremely well with one another. In 1.3 C14 does not couple to phosphorous, but C11 shows a $^3J(^{31}\text{P}-^{13}\text{C})$ of 6.6 Hz. Whereas in 1.2 a small coupling is observed for C12 and C13 (ca. 1.5 Hz), in 1.3 neither C12 nor C13 provide coupling information. On the other hand, in 1.2, C15 shows

$^3J(^{31}\text{P}-^{13}\text{C}) = 0.0 \text{ Hz}$, whereas in 1.3 $^3J(^{31}\text{P}-^{13}\text{C}) = 2.2 \text{ Hz}$. For C10 in 1.3, a 2J value of 8.0 Hz is found. These differences in the 3J values between 1.2 and 1.3 are not easily explained. However, it is a well established fact that small differences in "through-space" interactions between ^{31}P and other nuclei, X, as determined by steric effects (in this case a PBr_2 -*versus* a PCl_2 -unit at C9) can result in significant differences in the magnitudes of ^{31}P -X coupling constants. This effect most likely results from increasing or decreasing interaction between the atom X and the phosphorous lone pair¹³). This line of argumentation can furthermore be used to explain why C11 shows such a strong 3J coupling (6.6 Hz in 1.3, 7.3 Hz in 1.2), whereas C15 couples only weakly ($^3J = 2.2 \text{ Hz}$ in 1.3) if at all. C11 is located in the vicinity of the phosphorous lone pair and couples more strongly *via* a through-space interaction.

1.2.1.1 Spectroscopic Data

The similarities between the two compounds 1.2 and 1.3 are further borne out by the near-identical positions of the ^{13}C -NMR signals in the tmp region. ^{11}B -, ^1H -, and ^{13}C -NMR data for 1.2 and 1.3 are listed in Tables 1, 2, and 3, respectively.

Table 1: ^{11}B - and ^{31}P -NMR Data of the Addition Products 1.2-1.3, 1.6-1.8, and 1.11-1.12 (in ppm; half-widths in Hz; solvents: 1 = CDCl_3 , 2 = C_6D_6 , 3 = toluene/ C_6D_6 ca. 10/1)

Add. of	Nr.	$\delta^{11}\text{B}$	$h_{1/2}$	Solvent	$\delta^{31}\text{P}$	$\delta^{31}\text{P}(\text{S.M.})^*$
PCl_3	<u>1.2</u>	42.6	700	1	190	220
PBr_3	<u>1.3</u>	43.0	550	2	200	228
$(\text{NMe}_2)\text{PCl}_2$	<u>1.6</u>	45.2	510	2	150	166
PhPCl_2	<u>1.7</u>	44.5	560	1	121	160
BzPCl_2	<u>1.8</u>	45.4	710	1	140	180
Me_2PCl	<u>1.11</u>	48.4	330	3	- 4	
Ph_2PCl	<u>1.12</u>	44.3	720	2	52	84

* Lit.: 7-8

Table 2: ^1H -NMR Data of the Addition Products 1.2-1.3, 1.6-1.8, and 1.12 (in ppm; solvents as in Table 1)

Add. of	Nr.	CH_3 (tmp)	CH_2 (tmp)	arom. H (fluorene)	other
PCl_3	<u>1.2</u>	0.90	1.40-1.44	7.18-7.43(4H) 7.69-7.90(4H)	--
PBr_3	<u>1.3</u>	0.95	1.14-1.18	7.15-7.34(4H) 7.60-7.70(2H) 8.13-8.23(2H)	--
$(\text{NMe}_2)\text{PCl}_2$	<u>1.6</u>	0.93	1.32	6.99-7.30(4H) 7.45-7.55(2H) 8.03-8.15(2H)	1.42 (NM)
PhPCl_2	<u>1.7</u>	0.76	1.04-1.15	7.10-7.35(4H) 7.84-8.07(4H)	5.97- 6.65 (Ph)
BzPCl_2	<u>1.8</u>	0.76	1.04-1.15	6.88-7.20(4H) 7.35-7.51(2H) 7.86-8.00(2H)	1.56- 6.47 6.69 (Ph)
Ph_2PCl	<u>1.12</u>	1.36	1.64-2.07	7.24-7.47 7.50-7.78 8.18-8.29 ^b	--

a. $\text{CH}_2\text{-Ph}$: $^2J(^{31}\text{P}-^1\text{H}) = 13 \text{ Hz}$

b. Phenyl and fluorenyl protons overlap. Total integral: I = 18H

The numbering scheme for the tmp and fluorenyl moieties is given in Fig. 1.1 and will be used in all tables and discussions which follow.

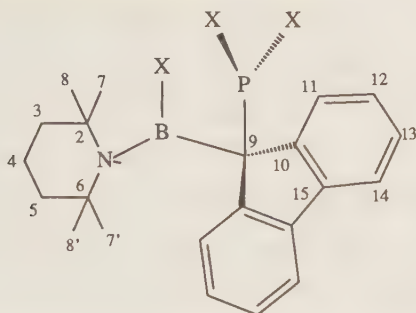


Fig. 1.1: Numbering scheme in PX_3 addition products for the ^{13}C -NMR spectra in Table 3b. The same scheme will be used throughout this work.

Table 3: ^{13}C -NMR Data of the Addition Products 1.2-1.3, 1.6-1.8, and 1.12 (in ppm; solvents as in Table 1; numbering scheme as in Fig. 1.1)

Table 3a: ^{13}C -Resonances of the tmp ring

<u>Nr.</u>	<u>C4</u>	<u>C7/8</u>	<u>C3/5</u>	<u>C2/6</u>	<u>other</u>
<u>1.2</u>	14.4	32.0	36.3	57.7	--
<u>1.3</u>	14.7	32.5	36.5	58.8	--
<u>1.6</u>	15.4	29.3	36.5	57.2	38.7 ^a
		35.9			(N(CH ₃) ₂)
<u>1.7</u>	14.9	28.9	36.9	57.4	--
		35.5			
<u>1.8</u>	14.7	29.5	36.7	57.4	36.9 ^b
		34.7			(CH ₂ -Ph)
<u>1.12</u>	14.9	31.9	37.3	57.5	--

a. $^2J(^{31}P-N-^{13}C) = 24.0$ Hz

b. $^1J(^{31}P-^{13}C) = 46.0$ Hz

Table 3b: ^{13}C -Resonances of the fluorene ring ($^{\text{f}}\text{J}(^{31}\text{P}-^{13}\text{C})$ values in brackets, given in Hz)

<u>Nr.</u>	<u>C9</u>	<u>C10</u>	<u>C15</u>	<u>C11</u>	<u>C12</u>	<u>C13</u>	<u>C14</u>	<u>other</u>
<u>1.2</u>	n.o.	142.8 (8.1)	141.6	125.3 (7.3)	127.0 (1.5)	127.4 (1.5)	120.1	--
<u>1.3</u>	70.0	144.5 (8.8)	142.1 (2.2)	125.4 (6.6)	128.4 (1.5)	127.5	120.5	--
<u>1.6</u>	n.o.	144.9 145.2	141.1 141.3	125.3 125.6	126.2 126.9	127.3 127.5	120.1 120.5	--
<u>1.7^a</u>	n.o.	145.6 145.8	--	--	--	--	119.4 120.0	--
<u>1.8^a</u>	n.o.	146.8 146.9	--	--	--	--	120.1 120.3	--
<u>1.12</u>	n.o.	146.8 (1.5)	140.5 (1.8)	125.9 (6.2)	125.7	125.7	119.5	b

n.o. = not observed because of signal broadening from quadrupolar coupling (boron-bound C-atoms)

a. Because of the complexity of the aromatic region, unambiguous assignment of the ^{13}C -NMR signals for C11-C13 and C15 could not be made.

b. 126.4 (m-phenyl, $J = 6.2$ Hz)
128.2 (p-phenyl)
134.8 (o-phenyl, $J = 22.0$ Hz)
136.4 (i-phenyl, $J = 30.4$ Hz)

1.2.1.2 X-Ray Crystal Structure of 1.2

Crystals of 1.2 suitable for an X-ray crystal structure were obtained from a hexane:toluene mixture (ca. 2:1) at -20°C . 1.2 crystallizes in the triclinic system, space group P1, with $Z = 4$. The crystal structure confirms the description from NMR data of 1.2 as the product of the addition of PCl_3 across the $\text{B}=\text{C}$ double bond. An ORTEP plot of 1.2 is given in Fig. 1.2. Bond lengths and bond angles are given in Tables 4 and 5, respectively.

The B-C bond length of $1.617(4)$ Å corresponds to a B-C single bond. The B-N bond length of $1.394(4)$ Å represents a significant amount of double bond character. In $\text{tmpB}=\text{CR}_2$, the B-N bond length was found to be $1.353(3)$ Å and the

B-C bond length was 1.424(3) Å⁶. Thus, in 1.2, the B-C and B-N bonds are lengthened by 0.20 Å and 0.04 Å, respectively.

The P-Cl bond lengths are found to be 2.064(1) Å and 2.077(1) Å, the P-C bond length is 1.919(3) Å. The geometry at phosphorous can be described as a distorted tetrahedron with the Cl-P-Cl angle (98.5(1)°) slightly smaller than the Cl-P-C angles (100.4(1)° and 101.4(1)°).

The geometry at B is a strongly distorted trigonal planar arrangement. C(1), B, Cl, and N are found to lie in a plane, but the bond angles at B differ dramatically: C(1)-B-N = 132.5(2)°, Cl-B-N = 118.4(2)° and Cl-B-C = 109.1(2)°.

The fluorene ring system is found to be almost planar with the planes of the two six-membered rings forming an angle of 3.8° relative to each other.

The geometry at the boron-bound C-atom is found to be a distorted tetrahedron: P-C(1)-B = 106.8(2)°, P-C(1)-C(2) = 99.4(2)°, P-C(1)-C13 = 110.7(2)° and C(2)-C(1)-C(13) = 102.2(2)°. The C(1)-C(2) bond length of 1.527(3) Å is nearly identical to the C(1)-C(13) bond length of 1.516(3) Å, considering standard deviations. Thus, the large difference in bond angles at C(1) from the P-atom to the two six-membered rings (defined by C(2) and C(13)) is due to the lone pair at phosphorous. The larger angle is found for the ring situated in a *trans* position to the lone pair on phosphorous.

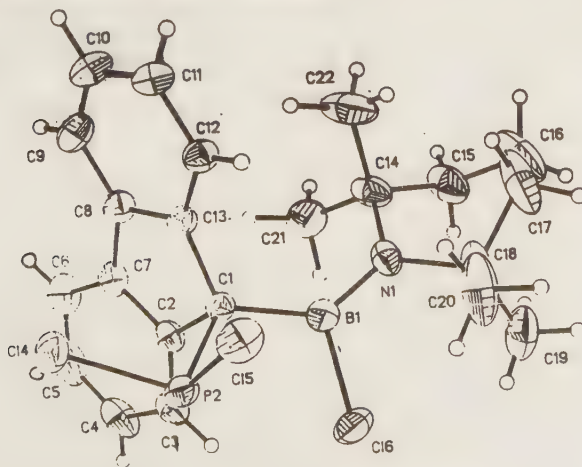


Fig. 1.2: ORTEP Plot of the compound 1.2

Table 4: Selected Bond Lengths (in Å) and Angles (in degrees) in 1.2. The atoms are labeled as in the ORTEP Plot (Fig. 1.2)

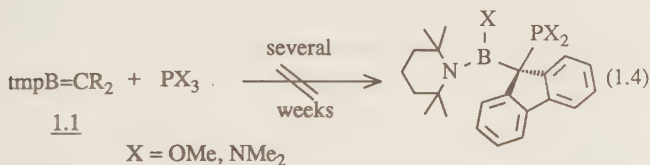
P(2)	-C(1)	1.919(3)	Cl(6)	-B(1)	1.834(3)
P(2)	-Cl(4)	2.064(1)	P(2)	-Cl(5)	2.077(1)
C(1)	-C(2)	1.527(3)	C(1)	-C(13)	1.516(3)
C(1)	-B(1)	1.617(4)	C(2)	-C(3)	1.397(3)
C(2)	-C(7)	1.397(4)	C(3)	-C(4)	1.398(4)
C(4)	-C(5)	1.368(5)	C(5)	-C(6)	1.379(4)
C(6)	-C(7)	1.386(4)	C(7)	-C(8)	1.461(3)
C(8)	-C(13)	1.405(3)	C(8)	-C(9)	1.389(4)
C(9)	-C(10)	1.376(4)	C(10)	-C(11)	1.381(4)
C(11)	-C(12)	1.386(4)	C(12)	-C(13)	1.384(3)
B(1)	-N(1)	1.394(4)	N(1)	-C(14)	1.539(4)
N(1)	-C(18)	1.529(4)	C(14)	-C(15)	1.544(5)
C(14)	-C(21)	1.505(5)	C(14)	-C(22)	1.525(5)
C(15)	-C(16)	1.503(6)	C(17)	-C(18)	1.546(6)
C(18)	-C(19)	1.545(5)	C(18)	-C(20)	1.533(6)

Table 5: Selected Bond Angles (in degrees) in 1.2. The atoms are numbered as in the ORTEP Plot (Fig. 1.2)

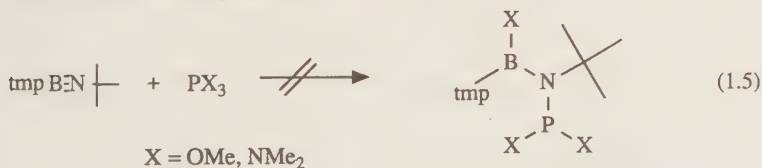
Cl(4)	-P(2)	-Cl(5)	98.5(1)	Cl(4)	-P(2)	-C(1)	100.4(1)
Cl(5)	-P(2)	-C(1)	101.4(1)	P(2)	-C(1)	-C(2)	99.4(2)
P(2)	-C(1)	-C(13)	110.7(2)	C(2)	-C(1)	-C(13)	102.2(2)
P(2)	-C(1)	-B(1)	106.8(2)	C(2)	-C(1)	-B(1)	116.2(2)
C(13)	-C(1)	-B(1)	119.7(2)	C(1)	-C(2)	-C(3)	129.6(2)
C(1)	-C(2)	-C(7)	109.9(2)	C(3)	-C(2)	-C(7)	120.4(2)
C(2)	-C(3)	-C(4)	117.7(3)	C(3)	-C(4)	-C(5)	121.5(3)
C(4)	-C(5)	-C(6)	121.0(3)	C(5)	-C(6)	-C(7)	119.0(3)
C(2)	-C(7)	-C(8)	109.1(2)	C(7)	-C(8)	-C(13)	108.6(2)
C(1)	-C(13)	-C(12)	130.0(2)	Cl(6)	-B(1)	-C(1)	109.1(2)
Cl(6)	-B(1)	-N(1)	118.4(2)	C(1)	-B(1)	-N(1)	132.5(2)
B(1)	-N(1)	-C(14)	122.3(2)	B(1)	-N(1)	-C(18)	120.6(3)
C(14)	-N(1)	-C(18)	116.8(2)	N(1)	-C(14)	-C(15)	106.5(3)
N(1)	-C(14)	-C(21)	109.7(3)	N(1)	-C(14)	-C(22)	113.5(3)
N(1)	-C(18)	-C(17)	108.2(3)	N(1)	-C(18)	-C(19)	112.4(3)

1.2.2 Reaction of $\text{tmpB}=\text{CR}_2$ with Trimethoxy- and Tris(dimethylamino)-phosphane

Combining equimolar amounts of P(OMe)_3 or $\text{P(NMe}_2)_3$ and $\text{tmpB}=\text{CR}_2$ at room temperature in toluene results in no immediate reaction. Because heating to reflux results in the formation of an oxidation product of 1.1, the structure of which has never been defined, but which has been observed by many researchers^(6),14)-16), the solutions were not refluxed but stirred for long periods. Though a small amount of a new boron-containing product ($\delta^{11}\text{B} = 36$ ppm) could be detected, the ^{31}P -NMR spectra clearly indicated only starting material in both cases. Use of excess PX_3 ($\text{X} = \text{OMe}, \text{NMe}_2$) could not bring about the desired reaction (eq. 1.4).



This failure on the parts of P(OMe)_3 and $\text{P(NMe}_2)_3$ to yield 1:1 adducts with 1.1 can be compared to their failure to yield analogous adducts with the amino-imino-borane, $\text{tmpB}=\text{N}^t\text{Bu}$ (eq. 1.5).

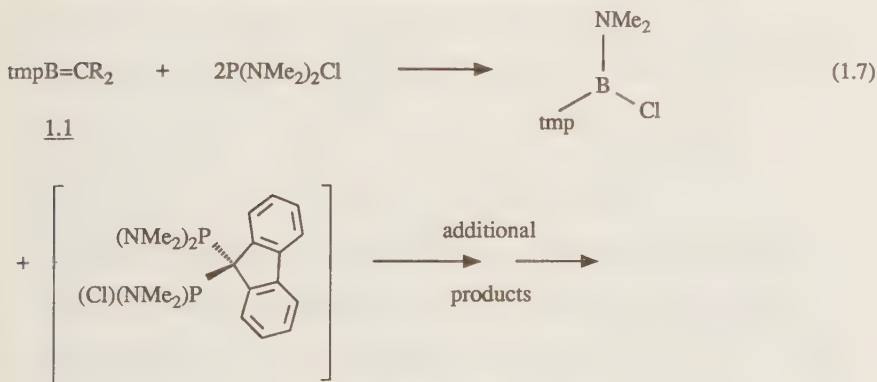


In these latter cases, refluxing the reaction mixtures merely resulted in a more rapid dimerization of the imino-borane to the corresponding diazaboretidine⁽⁵⁾. The reason for the failed reactions is most likely the lack of Lewis-acidic character exhibited by both P(OMe)_3 and $\text{P(NMe}_2)_3$. Relationships between reactivity towards $\text{tmpB}=\text{N}^t\text{Bu}$ and Lewis acidity have been well established^(3),5). This relationship will prove to be important for $\text{tmpB}=\text{CR}_2$ as well (see below).

not possible. It should, however, be mentioned that a similar, for the most part uncharacterizable, reaction mixture resulted from the reaction of $\text{tmpB}\equiv\text{N}^t\text{Bu}$ and $\text{P}(\text{OMe})_2\text{Cl}^{(5)}$.

1.2.4 Reaction of $\text{tmpB}=\text{CR}_2$ with Bis(dimethylamino)chlorophosphane

Stirring equimolar quantities of $\text{tmpB}=\text{CR}_2$ and $\text{P}(\text{NMe}_2)_2\text{Cl}^{(19)}$ in toluene for several hours results in the formation of a new boron-containing product, 1.5, at $\delta^{11}\text{B} = 31.6 \text{ ppm}$ ($h_{1/2} = 80 \text{ Hz}$). One-half (by ^{11}B -NMR) of the starting material, 1.1, remains but a second equivalent of $\text{P}(\text{NMe}_2)_2\text{Cl}$ can then be added, which results in complete reaction to 1.5, according to equation 1.7.

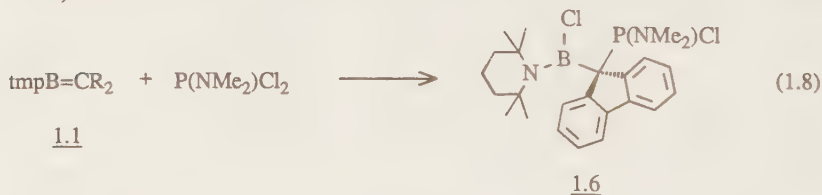


Though the reaction path must remain hypothetical because the products could not be isolated, the suggested pathway can be inferred from 1) the stoichiometry of the reaction: an exactly 1:1 reaction left half of the starting material 1.1 unreacted; and 2) the ^{11}B -chemical shift and half-width correspond to a $\text{tmp}(\text{amino})\text{chloroborane}$. (For comparison, $\text{tmpB}(\text{Cl})(\text{NHCMe}_3)$: $\delta^{11}\text{B} = 30.4 \text{ ppm}$, $h_{1/2} = 130 \text{ Hz}^{(20)}$). As was the case with the reaction of 1.1 with $\text{P}(\text{OMe})_2\text{Cl}$, the ^{31}P -NMR spectrum is of little help in elucidating the reaction path. Several signals are obtained (more than 10 different signals between -30 ppm and 200

ppm), with none being dominant. Thus, the presence of a single secondary product as indicated in equation 1.7 is merely a formalism; in fact, the reaction is much more complex in nature. Once again, this fits in well with the pattern established for $\text{tmpB}=\text{N}^t\text{Bu}$, for which the reaction with $\text{P}(\text{NMe}_2)_2\text{Cl}$ led to a mixture of products, none of which could be isolated or fully characterized²¹⁾.

1.2.5 Reaction of $\text{tmpB}=\text{CR}_2$ with (Dimethylamino)dichlorophosphane

The reaction of $\text{tmpB}=\text{CR}_2$ with $\text{P}(\text{NMe}_2)_2\text{Cl}_2$ ¹⁹⁾ in toluene produces the compound 1.6 in good yield as a crystalline solid, stable at room temperature (eq. 1.8).



The question posed in section 1.2.3 regarding which of two functional groups, X or X', on a phosphorous atom will preferably migrate to boron (a question which proved unanswerable for the cases of the bis(amino)- or -bis(methoxy)chlorophosphanes because of the unexpected complexity of the reactions) can now be answered. The chlorine atom migrates to boron, as can be shown by ¹¹B-, ³¹P-, ¹H- and ¹³C- NMR. The NMR data for 1.6 are given in Tables 1-3 (see above, section 1.2.1).

The ¹¹B-NMR spectrum of 1.6 provides the first indication. The shift of $\delta^{11}\text{B} = 45.2$ ppm ($h_{1/2} = 510$ Hz) clearly corresponds to a (organyl)(tmp)borane, found only 2 ppm downfield from the PCl_3 adduct, 1.2. This slight downfield shift in 1.6 most probably results from the poorer $\text{p}\pi\text{-p}\pi$ overlap between boron and the nitrogen of tmp as a result of steric constraints imposed by one of the chlorine atoms on phosphorous being replaced by a NMe_2 group. As further indication that

Cl and not NMe₂ is transferred, the ¹¹B-NMR spectrum of 1.6 can be compared with the HNMe₂ adduct of 1.1, for which a ¹¹B-chemical shift of 37.9 ppm was found²²). This is clearly far enough upfield from the product 1.6 to rule out a similar structure.

The ³¹P-NMR spectrum also lends supports to the proposed structure 1.6. It contains a single signal at δ³¹P = 149.5 ppm. This is well within the region expected for (amino)(organyl)chlorophosphanes (e.g. δ³¹P = 151.2 for tmpB(Cl)N^tBuP(Cl)ⁱPr²³). As with 1.2 and 1.3, the ¹H-NMR spectrum of 1.6 again demonstrates the anisotropic effect of the fluorenyl group, with the methyl groups of tmp being found at δ¹H = 0.93 ppm. The other interesting feature of the ¹H-NMR spectrum is the high-field shift of the methyl groups of the NMe₂ moiety. This results from the proximity of NMe₂ to the fluorenyl ring system. The upfield shift is quite large: a broad singlet corresponding to 6H is found at δ¹H = 1.42 ppm; "normal" NMe₂ protons are found at 2.7 ppm. (For comparison, the ¹H-NMR spectrum of the HNMe₂ adduct of 1.1 indicated the presence of one NMe₂ methyl group which was affected by this anisotropic effect and one which was not affected. The protons not affected were found at δ¹H = 2.68 ppm. Those influenced by the ring current fell between 1.40 and 1.53 ppm²²).

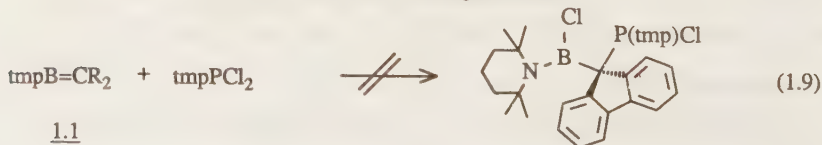
The ¹³C-NMR spectrum of 1.6 contains several interesting features. The signal for the C-atoms of the tmp methyl groups is split, and two different signals are found at δ¹³C = 35.9 ppm. This splitting is a diastereotopic effect from the neighboring chiral phosphorous atom. It is also observed in the MePCl₂ insertion product of 1.1 (δ¹³C /tmpCH₃ = 29.3, 34.7 ppm²²) and in the ⁱPrPCl₂ adduct (δ¹³C = 29.1, 35.5 ppm¹¹). The ¹³C-NMR signal for the N(CH₃)₂ group at 38.7 ppm is distinguishable from the ¹³C-NMR signal for C3,5 of tmp because of the doublet which results from the ²J(³¹P-¹³C) value of 24 Hz. This value is well within the range expected for ²J(³¹P-¹³C) via a nitrogen atom (²J for P(NMe₂)₃ is 17 Hz²⁴). Furthermore, the ¹³C-NMR signal at δ¹³C = 38.7 ppm is in good agreement with that of the high-field shifted methyl group in the HNMe₂ adduct (δ¹³C = 36.2²²).

The interpretation of the signals in the aromatic region of the ¹³C-NMR spectrum of 1.6 presents more problems. The chirality of the phosphorous center

results in two sets of six signals for the fluorenyl group. Couplings to phosphorous cannot be determined. The coupled signals overlap to such an extent that an exact assignment is not possible except in a few cases. For example, C14, known not to couple strongly to phosphorous in 1.2 and 1.3 (see above, section 1.2.1), is found to be split into two signals which lie 16 Hz apart. Because this is much too large for a $^4J(^{31}\text{P}-^{13}\text{C})$ coupling constant, it can be assumed that the two signals at $\delta^{13}\text{C} = 120.1$ and 120.5 ppm correspond to C14 and C14'. For C11, assuming coupling, $J = 12$ Hz, a value which, based on 1.2 and 1.3, still seems large, but it might be acceptable. Similarly, the coupling to C10 would be 15 Hz, somewhat large for 2J , but still feasible. Otherwise, all J values would be much too large when compared to values from this work and the literature¹⁰⁾(see below, Chapter 2). Thus, the ^{13}C -NMR data are presented in Table 3b (see above, section 1.2.1) as two sets of signals, unless otherwise indicated.

1.2.6 Reaction with tmpPCl₂

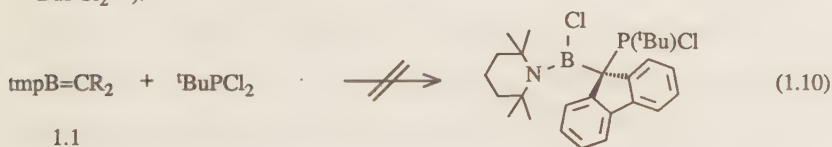
The 1:1 reaction of tmpPCl₂ and 1.1 fails to yield the addition products, even after 4 weeks stirring at room temperature (eq. 1.9). Though it was known that tmpPCl₂ is too bulky to add to tmpB≡N^tBu²³⁾, it was hoped, based on a successful experiment with a bulky (chloro)dioxaphospholane (see below, section 2.1.2), that a long reaction time would lead to product formation. tmpPCl₂ proved, however, to show no tendency to react. A ^{31}P -NMR spectrum of the reaction mixture after four weeks indicated only starting material.



1.2.7 Reaction with (Alkyl)phosphorous Dichlorides

1.2.7.1 With (^tButyl)phosphorous Dichloride

1.1 and ^tBuPCl₂ in a 1:1 mixture in toluene at room temperature do not react (eq. 1.10). Stirring for several days results in no change in the ¹¹B- and ³¹P-NMR spectra. Heating the mixture to reflux for several hours merely results in the formation of the oxidation product of 1.1 ($\delta^{11}\text{B} = 36$ ppm), whereas the ³¹P-NMR spectrum remains unchanged (one signal at $\delta^{31}\text{P} = 199$ ppm for ^tBuPCl₂²⁵).

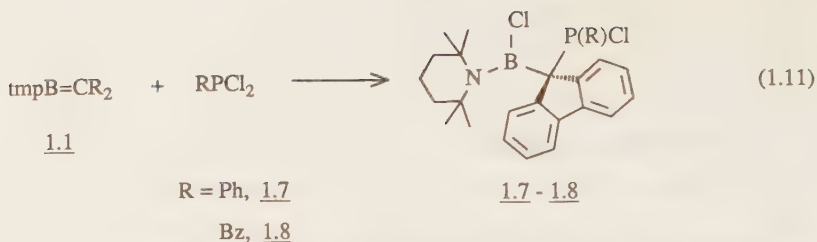


As with the reaction with tmpPCl₂, the reason for the failed reaction is most likely steric in nature. ^tBuPCl₂ similarly did not react with tmpB=^tBu, apparently because of steric reasons⁵.

1.2.7.2 With (Phenyl)- and (Benzyl)phosphorous Dichlorides

PhPCl₂ and BzPCl₂ react at room temperature with 1.1 to yield the expected products, 1.7 and 1.8, according to equation 1.11.

1.7 is isolated as an air-stable, colorless, analytically pure powder, only slightly soluble in aromatic solvents, though enough so to obtain NMR spectra from C₆D₆ solutions.



1.7 could also be characterized by mass spectroscopy at 70 eV. No parent peak is found at $m/e = 493$, but the $(\text{M-P(Ph)Cl})^+$ fragment is found at $m/e = 350$ (^{11}B , ^{35}Cl). Furthermore, the fragment $(\text{P(Ph)Cl})^+$ is found with 58% intensity at $m/e = 143$.

The NMR data for 1.7 and 1.8 are listed in Tables 1-3 (see above, section 1.2.1).

The ^{11}B -NMR spectrum contains one signal at $\delta^{11}\text{B} = 44.5$ ppm, corresponding to Cl(R)BNR_2 -type compounds. The ^{11}B -chemical shift of 1.7 is found at slightly lower field than that of 1.2, presumably for steric reasons (ie. decreased $p\pi$ - $p\pi$ overlap).

The ^{31}P -NMR spectrum also supports the structure suggested for 1.7. The signal at $\delta^{31}\text{P} = 121$ ppm represents an upfield shift of 39 ppm, similar in magnitude to $\Delta\delta^{31}\text{P}$ found for other 1.1 insertion products of chlorophosphanes (see Table 1). The ^{31}P -NMR signal is, however, also significantly downfield from that of the (dialkyl)chlorophosphane, Me_2PCl ($\delta^{31}\text{P} = 96.5$ ppm)⁷, as expected for a phenyl(alkyl)chlorophosphane.

The ^1H -NMR spectrum of 1.7 indicates the anisotropic effect of the fluorenyl group on neighboring substituents: the tmp methyl groups are found at $\delta^1\text{H} = 0.91$ ppm and the phenyl protons from the PhPCl -moiety are found between 5.97 and 6.65 ppm, significantly upfield from normal "benzene"-type protons, usually found at 7.15 ppm. Otherwise the ^1H -NMR spectrum shows no unusual features.

The ^{13}C -NMR spectrum is indicative of a compound containing a chiral center attached to C9 of the fluorenyl ring-system. C7 and C8 of tmp are split into two signals at $\delta^{13}\text{C} = 28.9$ and 35.5 ppm. In addition, 30 different signals are

found in the aromatic region as a result of the chirality of the phosphorous center as well as of the coupling to phosphorous. As was the case with the similarly asymmetrical adduct 1.6, C14 and C14' can be assigned to specific signals because of their location at higher field as well as their negligible coupling constants, $^4J(^{31}\text{P}-^{13}\text{C}) = 0.0$ Hz. Two signals are also found for C10 and C10' of the fluorenyl group as a result of the lack of symmetry. The *ipso*-C atom of the phenyl ring and C15 of the fluorenyl group are expected in approximately the same region (*ca.* 140 ppm; i-C in Ph-PMe₂ is found at $\delta^{13}\text{C} = 142.1$ ppm²⁶). Thus their signals cannot be unambiguously assigned.

The compound 1.8 has spectral features similar to those of 1.7. The ¹¹B-NMR spectrum of 1.8 contains one signal at $\delta^{11}\text{B} = 45.4$ ppm, almost in the same position as the signal for 1.7.

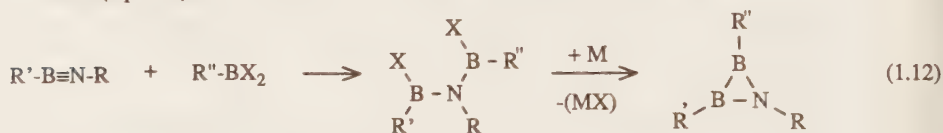
The ³¹P-NMR spectrum contains one signal at $\delta^{31}\text{P} = 139.6$ ppm, 40.4 ppm upfield from the starting material²⁶), thereby fitting in with the series of $\Delta\delta^{31}\text{P}$ found for similar adducts, esp. 1.7 (see table 1, section 1.2.1).

The ¹H-NMR spectrum of 1.8 indicates an even larger high-field shift for the tmp methyl protons ($\delta^1\text{H} = 0.76$ ppm) than is found in 1.2 - 1.7. The benzyl protons are found at $\delta^1\text{H} = 1.56$ ppm, upfield from the location of non-shielded benzyl protons (*ca.* 2.3 ppm). Furthermore, a $^2J(^{31}\text{P}-^1\text{H})$ coupling of 13 Hz is observed. This agrees well with the value found in the MePCl₂ addition product, for which $^2J(^{31}\text{P}-^1\text{H}) = 15$ Hz²²). It also lies between the values for MePCl₂ and Me₂PCl ($^2J(^{31}\text{P}-^1\text{H}) = 17.6$ Hz and 8.4 Hz, respectively)²⁷). The phenyl protons are also shielded by the fluorenyl group, as was the case in 1.7.

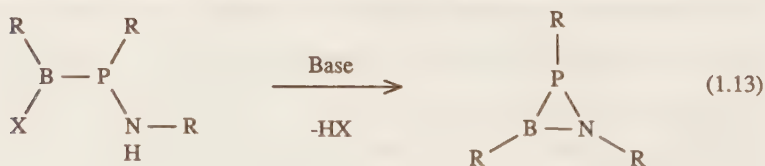
The ¹³C-NMR spectrum contains five signals for the tmp ring, indicating the presence of the chiral phosphorous center. In addition, the benzyl C-atom is found at $\delta^{13}\text{C} = 36.9$ ppm with a $^1J(^{31}\text{P}-^{13}\text{C})$ coupling constant of 46.0 Hz. This is nearly identical to $^1J(^{31}\text{P}-^{13}\text{C})$ found for the methyl group in the insertion product of MePCl₂ and 1.1 ($^1J = 44.3$ Hz⁶) as well as in MePCl₂ itself²⁸). As in 1.7, the complexity of the aromatic region does not allow for a reasonable assignment of the ¹³C-NMR signals.

1.2.7.2.1 Reaction of 1.8 with $\text{NaN}(\text{SiMe}_3)_2$

One of the main interests in the synthesis of compounds containing multiple bonds between boron and carbon or boron and nitrogen stems from their potential use as building blocks in the synthesis of small rings. Dirschl, *et al.*²⁹⁾ have synthesized a series of B_2N -rings by dehalogenation of diborylamines obtained *via* the addition of (alkyl)boron dihalides across the boron-nitrogen triple bond (eq. 1.12).



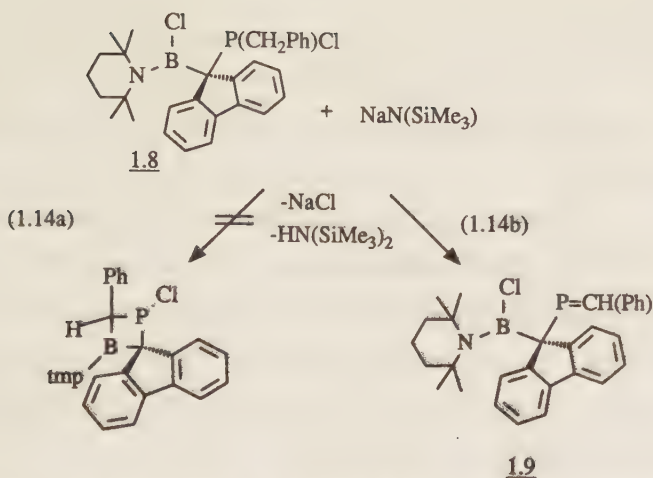
Kölle²³⁾ proposed another strategy for the synthesis of small phosphorous-containing heterocycles (eq. 1.13) involving dehydrohalogenation.



It was hoped that reaction of 1.8 with a bulky base such as $\text{NaN}(\text{SiMe}_3)_2$ would yield the otherwise inaccessible 4-membered BCPC-ring (as in eq. 1.14a). However, elimination of HX leads to the phosphaehtene 1.9 (eq. 1.14b).

The reaction was monitored by ^{11}B - and ^{31}P -NMR. As expected for 1.9, the ^{11}B -NMR signal did not change drastically ($\delta^{11}\text{B} = 38.3$ ppm) from the starting material 1.8, but the ^{31}P -NMR signal underwent a shift to much lower field (to $\delta^{31}\text{P} = 290$ ppm, from $\delta^{31}\text{P} = 140$ ppm for 1.8) as would be expected for $\text{RP}=\text{CR}_2'$ systems³⁰⁾.

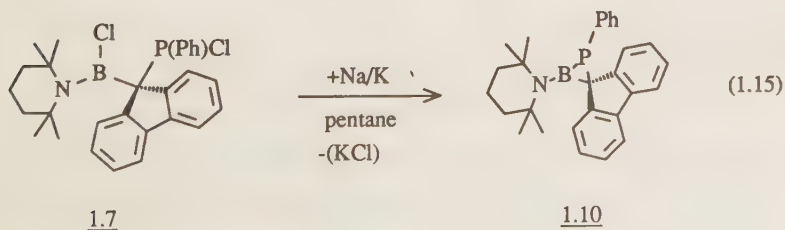
Addition of (dibenzyl)chlorophosphane to 1.1, followed by reaction with



NaN(SiMe₃)₂ should circumvent the problem of elimination at phosphorous and thereby yield the desired 4-membered ring. However, this pathway was not investigated in the course of this research.

1.2.7.2.2 Dehalogenation of 1.7 with Na/K alloy³¹⁾

Azaphosphaboriridines are accessible *via* dehalogenation reactions analogous to those which yield azadiboriranes³⁰⁾. Siebert³²⁾, *et al.* could similarly synthesize diboriranes, i.e. a six-membered B₄C₂-ring, *via* dehalogenation of a bis[amino(chloro)boryl]methane. Based on this methodology, it was hoped that 1.7 could be dehalogenated with Na/K in pentane to the phosphaborirane 1.10 (eq. 1.15),

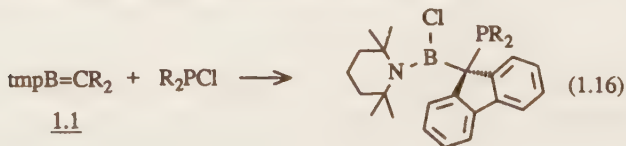


rather than to the six-membered ring, because of the bulk of the tmp group at boron. The correlation between the use of tmp-substituted borane precursors and intramolecular ring closure has been well established for diazaboridines and azaboridines³³⁾.

After stirring 1.7 in pentane for 24h in the presence of Na/K alloy, the ¹¹B-NMR spectrum indicated reaction to a new product at $\delta^{11}\text{B} = 38$ ppm. ³¹P-NMR also showed the presence of a new product at $\delta^{31}\text{P} = -47$ ppm. Though these data could well correspond to the desired 3-membered ring, product 1.10 could not be isolated from the reaction mixture. This system is currently being further investigated in our laboratories³¹⁾.

1.2.8 Reaction with (Dialkyl)chlorophosphanes

tmpB=CR₂ reacts with Me₂PCl and Ph₂PCl at room temperature in toluene to the products 1.11 and 1.12 according to equation 1.16.



R = Me, 1.11

Ph, 1.12

1.11 could only be characterized by its ¹¹B- and ³¹P-NMR spectra. The ¹¹B-NMR signal of $\delta^{11}\text{B} = 48.4$ ppm corresponds to a chloro(organyl)(tmp) borane in which the tmp ring, because of steric constraints, is twisted such that $\pi\text{-}\pi$ interaction between boron and nitrogen is greatly decreased. This would be expected for 1.11, in which the Me₂P-group represents the bulkiest substituent yet attached to C9 of the fluorenyl group and, therefore, the ¹¹B-NMR signal is the furthest downfield of all chlorophosphane adducts yet encountered (see above,

section 1.2.1, Table 1).

The ^{31}P -NMR signal of $\delta^{31}\text{P} = -3.8$ ppm is downfield from other trialkyl phosphines ($\delta^{31}\text{P}$ for $\text{PMe}_3 = -62$ ppm; $\text{PMe}(\text{Et})(\text{Ph}) = -33$ ppm³⁴) and could imply interaction between Cl and P. Unfortunately, 1.11 could not be isolated cleanly, and, therefore, its characterization must remain incomplete.

1.12, on the other hand, was isolated in good yield as an air-stable, crystalline solid and was fully characterized by analysis and NMR.

The NMR data of 1.11 and 1.12 are listed in Tables 1-3 (see above, section 1.2.1).

The ^{11}B -NMR signal of 1.12 at $\delta^{11}\text{B} = 44.3$ ppm indicates, as in 1.11, that the N-B π - π interaction is reduced compared to the PCl_3 adduct, 1.2. However, this signal is not as far downfield as that of 1.11, indicating the lesser steric bulk of phenyl groups compared to methyl, resulting from their planar nature and ability to take on a "face-to-face" orientation.

The ^{31}P -NMR shift of $\delta^{31}\text{P} = 52.0$ ppm is further downfield than would be expected if compared to PPh_3 ($\delta^{31}\text{P} = -5.9$ ppm³⁴). This could imply a slight interaction between the Cl-atom and phosphorous. The unusually broad ^{11}B -NMR signal ($h_{1/2} = 720$ Hz) could support this assumption.

The ^1H -NMR spectrum of 1.12 is similar to those of compounds 1.2-1.8, but the methyl protons of tmp are at slightly lower field than is found in the other products. This implies that the anisotropic effect of the fluorenyl group is less pronounced, most likely because the steric bulk at phosphorous prohibits the fluorenyl group from maximally shielding neighboring groups. This is further borne out by the non-shifted position of the phenyl protons ($\delta^1\text{H} = 7.24$ ppm and further downfield; exact assignment is difficult since the fluorenyl and phenyl protons overlap).

The ^{13}C -NMR spectrum of 1.12 indicates a symmetric, non-chiral environment: the tmp methyl groups are found as a single signal at $\delta^{13}\text{C} = 31.9$ ppm. This also allows coupling constants to be assigned, as well as ^{13}C -NMR shifts, to individual carbon atoms. The coupling to C11, $^3J(^{31}\text{P}-^{13}\text{C}) = 6.2$ Hz, is similar to that found in other chlorophosphane adducts of 1.1 for which coupling

constants could be unambiguously assigned (see Table 3 in section 1.2.1 and Chapter 2). The "through-space" nature of the coupling is also easily seen since, despite the substitution of alkyl groups for halogen atoms at the phosphorous atom, the J value remains relatively large. ^{31}P - ^{13}C couplings *via* bonds are known to be dependent on the substituents at the phosphorous atom, increasing as the electronegativities of the substituents increase³⁵. Hence, a very small $^2J(^{31}\text{P}, ^{13}\text{C})$ of 1.5 Hz is found for C10.

Other noteworthy features of the ^{13}C -NMR spectrum include the relatively large coupling to the i-C atom and the high-field shift of the o-C atom of the phenyl group. i-C is located at $\delta^{13}\text{C} = 136.4$ ppm with $^1J(^{31}\text{P}, ^{13}\text{C}) = 30.4$ Hz as compared to 12.5 Hz in PPh_3 . In $(\text{PPh}_3\text{Me})\text{I}$, 1J for the phenyl group is 88.6 Hz³⁵. This fact, along with the downfield ^{31}P -NMR shift and the broad ^{11}B -NMR signal could imply tetra-coordination at phosphorous. In addition, the o-C atom is found at $\delta^{13}\text{C} = 134.8$ ppm ($^2J = 22.0$ Hz). Although this 2J value is typical, the ^{13}C -NMR signal lies 4.7 ppm downfield from that found for o-C in $\text{Me}_2\text{P}(\text{C}_6\text{H}_5)$ ³⁶. Such a phenomenon is typical of tetra-coordination at phosphorous.

1.2.9 Reaction with PCl_5

The reaction of $\text{tmpBC}=\text{R}_2$ with PCl_5 was investigated to determine the difference in reactivity of 1.1 towards P(III) and P(V) halides. PCl_5 is known to exist in molecular form in benzene³⁷ and in ionic form as $(\text{PCl}_4)^+(\text{PCl}_6)^-$ in the solid state and in polar solvents³⁸. Thus, if a complex with 1.1 is formed, the question becomes whether it is ionic or molecular in nature (Figs. 1.a and 1.b).

If 1.1 is viewed simply as a Lewis acid, adduct formation to a complex of type 1b would be reasonable based on evidence from the literature: $(\text{PCl}_4)(\text{BCl}_4)$ ³⁸, $(\text{PCl}_4)(\text{TiCl}_5)$ ³⁹ and $(\text{PCl}_4)(\text{AlCl}_4)$ ⁴⁰ have all been synthesized from PCl_5 and the corresponding metal halide.

Reaction of 1.1 with an equimolar amount of PCl_5 in toluene over 12h

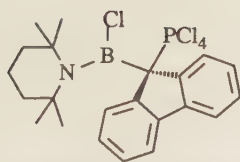


Fig. 1.a

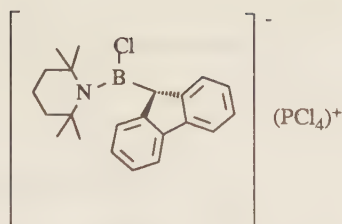
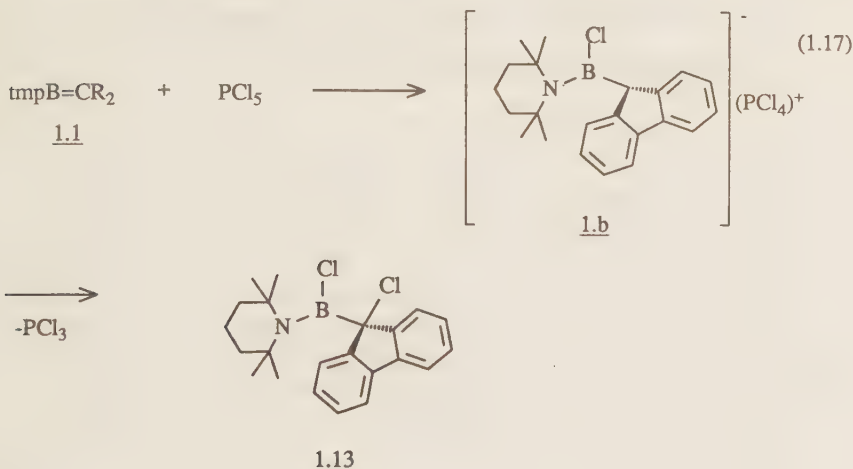


Fig. 1.b

resulted in reaction to a single product 1.13 with elimination of PCl_3 (by ^{31}P -NMR), as in equation 1.17.



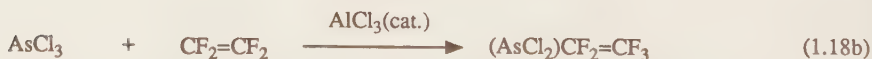
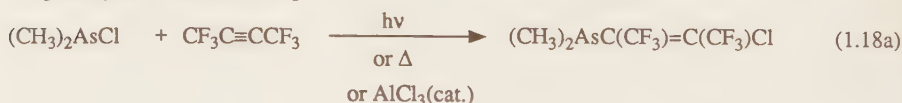
The product 1.13 could be characterized by ^{11}B -NMR ($\delta^{11}\text{B} = 43.0$ ppm) as a typical chloro(organyl)(tmp)borane. ^{31}P -NMR of the reaction solution clearly indicates the formation of only **one** reaction product at $\delta^{31}\text{P} = 220$ ppm (PCl_3)¹². The postulated intermediate 1b could not be detected (^{31}P -chemical shifts for $(\text{PCl}_4)^+$ vary with anion, but fall in the range of ca. 80 ppm³⁸). Attempts to isolate 1.13 by crystallization from toluene:hexane mixtures at low temperatures failed. 1.13 could be prepared by the direct reaction of 1.1 and Cl_2 gas, but as in the case of the PCl_5 reaction, the product could not be isolated. The ^{11}B -NMR data for the two reaction mixtures agree well with one another. In both cases, it was also observed that a light yellow solution with a fine white precipitate is obtained^{14b}.

1.2.10 Spectroscopic Data

NMR-data for the insertion products 1.2-1.13 are summarized in Tables 1-3 (see above, section 1.2.1).

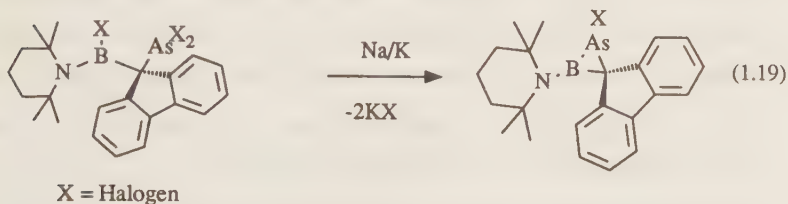
1.3 Reaction of tmpB=CR₂ With Non-cyclic Compounds of Arsenic(III), Antimony(III), and Bismuth(III)

Arsenic(III) halides are known to react with election-deficient alkenes and alkynes with insertion into the As-X bond. However, such reactions must often be catalyzed by AlCl₃, or carried out at extremely high temperatures or under photolytic conditions⁴¹⁾ (eq. 1.18).



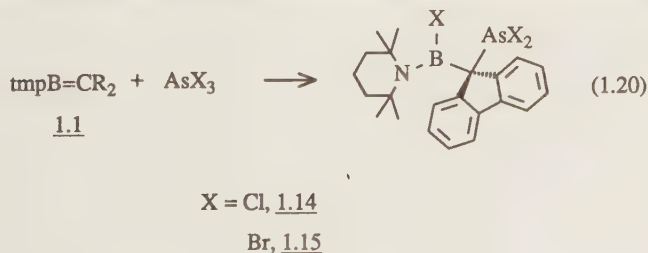
Metal-catalyzed addition of AsCl₃ to non-activated acetylenes is one of the most effective ways of generating (alkenyl)arsenic dichlorides⁴²⁾. In particular, this method has the advantage of stopping after a single addition. Syntheses of the (mono-alkyl)arsenic(III) halides by transmetallation reactions (involving the use of Grignard or alkyl-lithium reagents) are difficult to keep at the mono-substitution step, requiring careful control of the stoichiometry, reaction temperature and time, or the use of bulky alkylating reagents⁴³⁾. Because of the known tendency for As(III) halides to add across the B≡N triple bond in amino-imino-boranes⁵⁾ to yield boryl-substituted (amino)arsenic dihalides, and because of the fact that

tmpB=CR₂ was known to react neatly with P(III) halides, it was hoped that the corresponding As(III) halide addition products of 1.1 could be obtained. Such reactions would provide simple routes to boryl-substituted alkyl arsenic dihalides. Such products could potentially serve as starting materials for novel B-As-C-containing three-membered rings (eq. 1.19)⁴⁴.



1.3.1 Reaction with Arsenic Trihalides

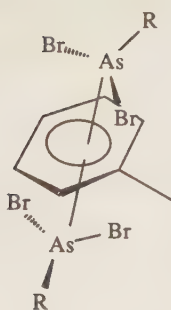
Stirring equimolar amounts of tmpB=CR₂ and AsX₃ (X=Cl, Br) in toluene results in very rapid reaction to the products 1.14 and 1.15 (according to equation 1.20). The reactions are complete after 2h as shown by ¹¹B-NMR and by the fact that a large amount of precipitate had formed. The compounds 1.14 and 1.15 are not very soluble in toluene. Recrystallization must be carried out from warm toluene:hexane mixtures. The compounds are found to decompose slowly at high temperatures in both the solid state and solution. However, storing a toluene solution of 1.14 at -20°C for 14 months resulted in no significant decomposition.



Both compounds were characterized by analysis, NMR and mass

spectroscopy. C-, H-, and N-analyses of 1.14 and 1.15 are presented in Table 6. The NMR data of 1.14 and 1.15 are given in Tables 7-9.

The largest fragments in the mass spectra of 1.14 and 1.15 are the $(M-AsX_2)^+$ peaks i.e. $(tmpB(X)(C_{13}H_8))^+$ (for $X = Cl$, $m/e = 350$, ^{11}B , ^{35}Cl ; for $X = Br$, $m/e = 394$, ^{11}B , ^{79}Br). The corresponding $(AsX_2)^+$ fragments are also found. Satisfactory analyses of the compounds 1.14 and 1.15 were thought at first to be unobtainable owing to their instability. Looking more carefully at the 1H -NMR spectra, however, toluene was found to be present in both cases. For $X=Cl$, one toluene molecule for three adduct molecules is present; for $X=Br$, one toluene to two adduct molecules is found, as determined by elemental analyses (see Table 6) and from 1H -NMR integrals. The nature of the toluene-adduct interaction is not yet known; however, it is suspected that toluene is weakly coordinated *via* an interaction between its π -cloud and As d-orbitals. In the case of 1.15, where the toluene:adduct ratio is 1:2, an inverse sandwich structure could be imagined:



Such complexes have been known for a long time and structures with various aromatic hydrocarbons as ligands have been determined⁴⁵⁾.

Table 6: Analyses (C, H, N) of the Addition Products 1.14-1.15 and 1.17-1.18 with Crystal Toluene

<u>Add. of</u>	<u>Nr.</u>	<u>Calc.(w/o tol.)</u>	<u>Calc.(w. tol.)</u>	<u>Found</u>	<u>Ratio^a</u>
AsCl ₃	<u>1.14</u>	C 53.22	55.43	55.11	3/1
		H 5.28	5.48	5.75	
		N 2.82	2.62	2.90	
AsBr ₃	<u>1.15</u>	C 41.95	45.31	45.42	2/1
		H 4.16	4.47	4.78	
		N 2.22	2.07	2.19	
SbCl ₃	<u>1.17</u>	C 48.63	50.91	50.56	3/1
		H 4.82	5.03	5.00	
		N 2.58	2.44	2.41	
SbBr ₃	<u>1.18</u>	C 39.05	43.88	44.35	3/4
		H 3.87	4.32	4.38	
		N 2.07	1.88	2.28	

a. Ratio = # molecules addition product/# molecules toluene

Table 7: ^{11}B -NMR Data of the Addition Products 1.14-1.15 and 1.17-1.19 (in ppm; half-widths in Hz; solvents numbered as in 1)

<u>Add. of</u>	<u>Nr.</u>	$\delta^{11}\text{B}$	$h_{1/2}$	<u>Solvent</u>
AsCl_3	<u>1.14</u>	41.6	370	1
AsBr_3	<u>1.15</u>	42.0	590	1
SbCl_3	<u>1.17</u>	43.8	450	1
SbBr_3	<u>1.18</u>	40.8	620	2
BiCl_3	<u>1.19</u>	37.8	720	1

Table 8: ^1H -NMR Data of the Products 1.14-1.15 and 1.17-1.18 (in ppm; solvents as in Table 7)

<u>Nr.</u>	<u>CH_3</u> (tmp)	<u>CH_2</u> (tmp)	<u>arom.H</u> (fluorene)
<u>1.14</u> ^a	0.92	1.23-1.42	7.07-7.11(4H) 7.24-7.41(2H) 7.71-7.86(2H)
<u>1.15</u> ^b	1.06	1.52-1.64	7.37-7.46(4H) 7.85-8.08(4H)
<u>1.17</u> ^a	1.01	1.49	7.16 7.32-7.42 7.82-7.98

a. Toluene signals also found but omitted for clarity. Integral corresponds to 3 molecules product/molecule toluene.

b. Toluene signals omitted; integral indicates 2 molecules product/molecule toluene.

Table 9: ^{13}C -NMR Data of the Products 1.14-1.15 and 1.17-1.19 (in ppm; solvents as in Table 7; numbering scheme as in Fig.1.1)

Table 9a: ^{13}C -Resonances of the tmp ring

<u>Nr.</u>	<u>C4</u>	<u>C7/8</u>	<u>C3/5</u>	<u>C2/6</u>
<u>1.14</u> ^a	14.4	32.0	36.2	57.9
<u>1.15</u> ^a	14.5	32.4	36.4	58.9
<u>1.17</u> ^a	14.7	32.2	36.3	58.3
<u>1.18</u> ^a	14.6	32.4	36.5	59.0
<u>1.19</u>	14.7	32.0 32.4	36.6	58.6

Table 9b: ^{13}C -Resonances of the fluorene ring

<u>Nr.</u>	<u>C9</u>	<u>C10</u>	<u>C15</u>	<u>C11</u>	<u>C12</u>	<u>C13</u>	<u>C14</u>
<u>1.14</u>	63.4	142.4	141.3	124.5	127.0	127.7	120.1
<u>1.15</u>	68.4	143.3	141.3	124.3	127.1	127.9	120.1
<u>1.17</u>	73.4	142.8	140.9	124.4	127.2	127.3	120.7
<u>1.18</u>	72.0	142.6	140.8	123.6	126.9	127.2	120.2
<u>1.19</u>	n.o.	---exact assignment not possible ^b ---					

n.o. = not observed: boron-bound C-atom

a. Toluene signals also found but omitted for clarity

b. See text.

The ^{11}B -chemical shifts of 1.14 and 1.15 are almost identical ($\delta^{11}\text{B} = 41.6$ ppm and 42.0 ppm, respectively) and are found in the region expected for chloro- or bromo(organyl)(tmp)boranes.

The ^1H -NMR spectra of 1.14 and 1.15 indicate not only their similarity to one another but also to the addition products of PCl_3 and PBr_3 (1.2 and 1.3). The high-field shift for the tmp methyl groups indicates that here, as well as in the phosphorous(III) halide addition products, there is a preferred conformation in which the MX_2 -unit is *cis* to the boron-bound X-atom, allowing for strong anisotropic interaction between tmp and the fluorenyl ring.

The ^{13}C -NMR spectra show no unusual structural features and rule out the possibility of any higher coordination of the fluorenyl ring to the arsenic atoms. In 1.15 quaternary C-atoms C10 and C15 are located at 141.3 and 143.3 ppm, respectively, at much lower field than the proton-bound ring carbon atoms. Such a marked difference in ^{13}C -NMR shifts in the fluorenyl region is characteristic of the fluorenyl ligand when bound only *via* C9 (η^1 -coordination)⁴⁶.

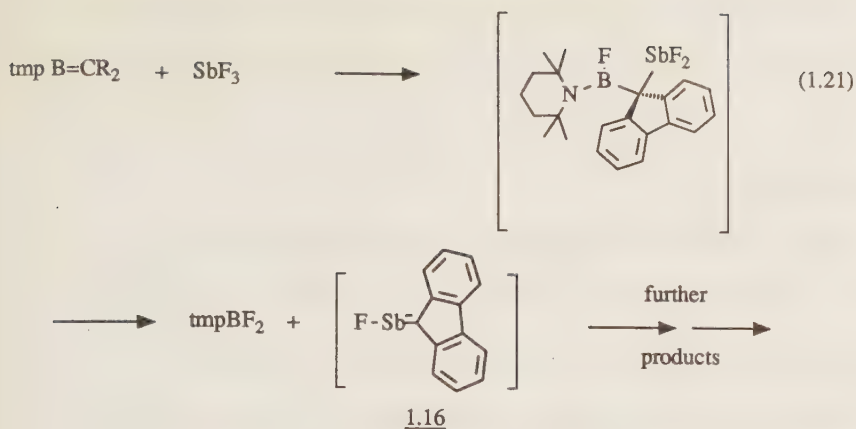
1.3.2 Reaction with Antimony Trihalides

1.3.2.1 Reaction with Antimony Trifluoride

As with the arsenic(III) halides, it was hoped that reaction of $\text{tmpB}=\text{CR}_2$ with the antimony analogues would lead to stable addition products: novel boryl-substituted (alkyl)antimony dihalides. It was known already that SbX_3 reacts to form stable complexes with $\text{tmpB}\equiv\text{N}^t\text{Bu}^{5)}$ for $\text{X} = \text{Cl}, \text{Br}$.

However, the question still arose of whether SbF_3 , commonly used as a fluorinating agent⁴⁷⁾ might yield a stable addition product with 1.1. No compound containing a M-F bond had yet been investigated.

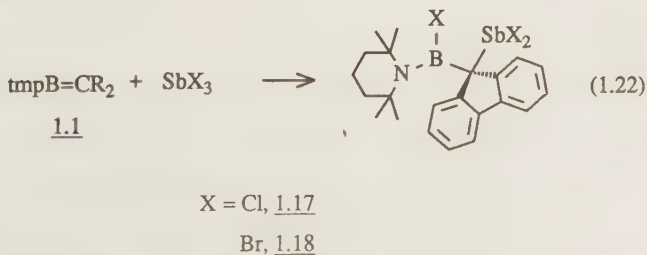
Stirring 1.1 and SbF_3 for 12h resulted only in the formation of tmpBF_2 , which could be characterized by ^{11}B -NMR ($\delta^{11}\text{B} = 17.1$ ppm, $h_{1/2} = 60$ Hz). The exact course of the reaction is not known, but one equivalent of SbF_3 sufficed, implying a path similar to equation 1.21.



Unfortunately, no product implying the involvement of 1.16 could be isolated *via* low-temperature crystallization.

1.3.2.2 Reaction with Antimony(III) Chloride and Bromide

In contrast to SbF_3 , both SbCl_3 and SbBr_3 react cleanly at room temperature with tmpB=CR_2 to yield the products 1.17 and 1.18 (eq. 1.22). As with 1.14 and 1.15, these two products are not very soluble in toluene and, therefore, one of the signs that reaction has occurred is their precipitation from toluene solutions at room temperature. The precipitated material can, however, be crystallized from warm toluene:hexane. The only disadvantage is slight decomposition of the products.



Compounds 1.17 and 1.18 were fully characterized by analysis, NMR and mass spectroscopy. Their NMR data are listed in Tables 7-9 (see above, section 1.3.1).

The mass spectra contain the $(M-SbX_2)^+$ fragments as the main peaks. No parent ion can be detected.

The 1H -NMR spectra of 1.17 and 1.18, as with 1.14 and 1.15, show no peculiar features, but do indicate the presence of toluene (1:3 for 1.17 and 3:4 for 1.18), which is supported by the analyses obtained (Table 6). The tendency for $SbCl_3$ and $SbBr_3$ to form complexes with aromatic hydrocarbons is well known (the so-called "Menschutkin" complexes)^(45c)-45e) and this effect could play a role in these cases as well. Other than the additional signals found for toluene, the compounds were spectroscopically clean.

The ^{11}B -NMR signals for 1.17 and 1.18 lie 0.6 ppm apart, comparable to the cases of 1.14 and 1.15, and correspond to $X(R)(tmp)boranes$ ($X = Cl, Br$).

The 1H -NMR spectrum of 1.17 substantiates the finding that the preferred conformation of $M(III)$ halide addition products ($M = P, As, Sb$) of 1.1 in general is that indicated in section 1.2.1 which allows for significant anisotropic shielding of the tmp methyl groups by the fluorenyl ring system. The tmp methyl proton resonance in 1.17 is $\delta^1H = 1.01$ ppm.

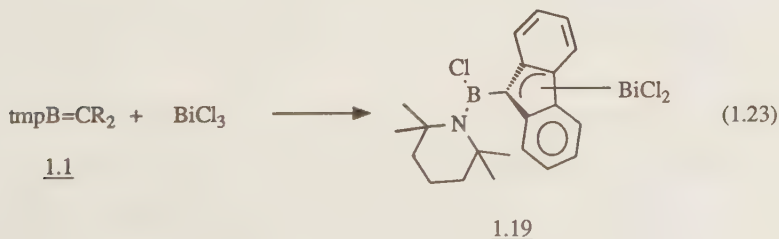
The ^{13}C -NMR spectra of 1.17 and 1.18 indicate that the tmp environment is similar to that found in the adducts of the phosphorous and arsenic trihalides. The fluorenyl region allows one to conclude that, despite antimony's larger atomic radius compared to As and P, and its greater tendency to form π -complexes with other aromatic systems⁽⁴⁸⁾, the Sb-atom is bound only to C9. The quaternary carbon atoms C10 and C15 are found between 140 and 144 ppm, far downfield from the benzene-like carbon atoms. As with the AsX_3 addition products, the coordination sphere of Sb in 1.17 and 1.18 has been increased through coordination of toluene molecules and not *via* higher coordination to the fluorenyl ring system. Such coordination at Sb could perhaps be obtained by halide abstraction, as Jutzi, *et al.* have shown in their successful synthesis of $[(n^5-C_5Me_5)_2M][BF_4]$ ($M = As$ and Sb)⁽⁴⁹⁾. This was, however, not attempted in the course of this work.

1.3.3 Reaction with Bismuth Trichloride

The heterogeneous reaction of BiCl_3 and $\text{tmpB}=\text{CR}_2$ yields 1.19, whose structure was ascertained from ^{11}B - and ^{13}C -NMR data (see above, section 1.3.1, Tables 7 and 9).

The product is an orange powder, insoluble in hexane and only slightly soluble in toluene, CHCl_3 or CH_2Cl_2 , yet which is soluble enough to obtain ^{11}B -NMR and ^{13}C -NMR spectra in CDCl_3 .

The ^{11}B -NMR signal of 1.19 at 37.8 ppm, together with the ^{13}C -NMR signals for the tmp methyl groups at 32.0 ppm and 32.4 ppm implies an increased $\text{B} \rightarrow \text{N}$ interaction and hence hindered rotation about the B-N bond. The bismuth atom, because of its larger size and greater tendency to increase its coordination sphere, could be coordinated to more than one carbon atom of the fluorenyl ligand. Such an interaction would decrease the fluorenyl ligand's ability to donate electron density to the boron atom, and thus encourage the increased $\text{B} \rightarrow \text{N}$ interaction. This idea is further supported by the high-field shifts observed for the fluorenyl quaternary carbon atoms (no C-atom is found at lower field than $\delta^{13}\text{C} = 129.4$ ppm). The large number of aromatic signals (exact assignment is not possible) most probably results from the bismuth atom sitting asymmetrically above the central fluorenyl ring (eq.1.23).



This relationship between the high-field ^{11}B -NMR shift and increased

coordination of the fluorenyl ligand will be further demonstrated (and more convincingly) at another point in this work (see Chapter 3).

1.3.4 Spectroscopic Data

^{11}B -NMR data for the series of compounds 1.14-1.19 are listed in Table 7; ^1H -NMR data are summarized in Table 8; ^{13}C -NMR data are summarized in Table 9 (see above, section 1.3.1).

Chapter 2:

Reactions of 9-Fluorenylidene-2,2,6,6-tetramethylpiperidino-borane with Cyclic Compounds of Phosphorous(III), Arsenic(III), and Antimony(III)

2.1 Reactions of $\text{tmpB}=\text{CR}_2$ with Cyclic Phosphorous(III) Compounds

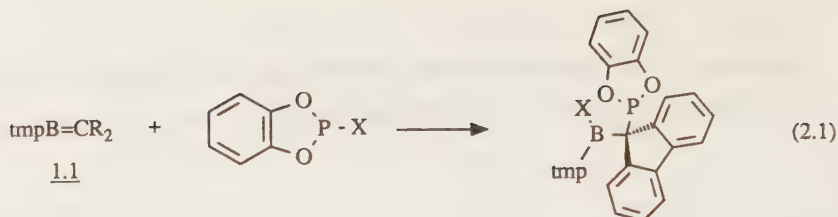
2.1.1 Reaction with 2-Halogeno-1,3,2-benzodioxaphospholane

As was discussed in sections 1.2.3 and 1.2.4, (dialkoxy)- and (diamino)phosphorous(III) halides failed to produce stable products with $\text{tmpB}=\text{CR}_2$, and this had also been previously observed with $\text{tmpB}\equiv\text{NR}^{11}$. However, Brandl found that through the use of cyclic phosphorous compounds, such as P-halo-dioxaphospholanes, stable insertion products with $\text{tmpB}\equiv\text{N}^t\text{Bu}$ were formed. It was hoped that a similar behaviour might be observed in analogous reactions with $\text{tmpB}=\text{CR}_2$.

The first examples studied were the addition reactions between $\text{tmpB}=\text{CR}_2$ and 2-chloro- and 2-bromo-1,3,2-benzo-dioxaphospholane. Equimolar amounts of the two starting materials in toluene solutions reacted rapidly at room temperature and the new products 2.1 and 2.2 were formed according to equation 2.1.

The products are crystalline solids whose structures as C-functionalized halogeno(organyl)(tmp)boranes could be proven by the spectroscopic data obtained.

The ^{11}B -NMR spectra of 2.1 and 2.2, with ^{11}B -NMR shifts of 45.7 and 46.0 ppm, respectively, correspond to chloro- and bromo(organyl)(tmp)boranes in which a slight downfield shift of ca. 3 ppm relative to the PCl_3 and PBr_3 adducts (1.2 and 1.3) indicates the presence of a bulky substituent at C9. This downfield shift has also been found for other P-functionalized addition products of P(III) halides, and probably results from out-of-plane twisting of the tmp ligand because



	X
<u>2.1</u>	Cl
<u>2.2</u>	Br

of steric interactions, as discussed in Chapter 1 (see Chapter 1, ref. 9). Furthermore, the ^{11}B -NMR shifts rule out the possibility that one of the oxygen atoms, and not the halogen atom, has migrated from phosphorous to boron. The ^{11}B -NMR signal of such an alkoxy(organyl)(tmp)borane would be found at much higher field. (Compare, for example, $\text{tmpB}(\text{OMe})(\text{C}_{13}\text{H}_{10})$, $\delta^{11}\text{B} = 34.3 \text{ ppm}^2$).

The ^{31}P -chemical shifts of 2.1 and 2.2 are almost identical ($\delta^{31}\text{P} = 192.5 \text{ ppm}$ for 2.1 and 192.8 ppm for 2.2). This is in marked contrast to the large difference ($\Delta\delta^{31}\text{P} = 23.9 \text{ ppm}$) found in the chemical shifts of the starting bromo- and chloro-compounds³. Had an oxygen and not a halogen atom migrated, the difference in ^{31}P -chemical shifts caused by the presence of a bromine *versus* a chlorine atom at phosphorous would still be found. This is, however, not the case.

The ^{31}P -chemical shift furthermore falls well within the region expected for a bis(alkoxy)(alkyl)phosphane. For example, $\text{MeP}(\text{OMe})_2$ has a ^{31}P -chemical shift of 200 ppm^4 . The ring strain caused by the presence of a five-membered ring is known to have little effect on ^{31}P -NMR shifts for three-coordinate phosphorous(III) compounds⁵.

The ^1H -NMR spectra of 2.1 and 2.2 indicate slightly less shielding of the tmp methyl groups by the fluorenyl ring system compared to the compounds described in Chapter 1 (in particular, 1.2 and 1.3). The phenyl protons are also slightly shielded, being found at $\delta^1\text{H} = 6.55 \text{ ppm}$ and $6.43\text{-}6.70 \text{ ppm}$ for 2.1 and 2.2, respectively. This can be explained by the close proximity of the benzo-ring

to the fluorenyl ring system.

The ^{13}C -NMR spectra of 2.1 and 2.2 contain no unusual features except the noticeable lack of coupling to the phosphorous center. Through-bond couplings are expected to be much smaller than for the PCl_3 and PBr_3 adducts 1.2 and 1.3 since the halogen atoms on phosphorous have been replaced by less electronegative oxygen atoms. The only coupling observed is a $^2\text{J}(^{31}\text{P}-\text{O}-^{13}\text{C})$ to the oxygen-bound carbon atoms of the benzo-ring in 2.1 ($^2\text{J} = 7 \text{ Hz}$). This is in good agreement with other $^2\text{J}(^{31}\text{P}-\text{O}-^{13}\text{C})$ coupling constants⁶.

The boron- and phosphorous-bound C-atom (C9) is found at $\delta^{13}\text{C} = 76.1 \text{ ppm}$ with $^1\text{J}(^{31}\text{P}-^{13}\text{C}) = 35 \text{ Hz}$. This coupling constant is consistent with other $^1\text{J}(^{31}\text{P}-^{13}\text{C})$ values and, in particular, is very similar to that found by Glaser²⁾ for C9 in the MePCl_2 insertion product of 1.1 ($^1\text{J} = 50 \text{ Hz}$).

The mass spectrum of 2.1 further supports the structural suggestion made on the basis of the NMR data. The parent peak expected at $m/e = 489$ (^{11}B , ^{35}Cl) is not found, but two fragments resulting from initial P-C9 bond rupture at $m/e = 350$ ($\text{tmpB}(\text{Cl})(\text{C}_{13}\text{H}_9)^+$) and $m/e = 139$ ($\text{C}_6\text{H}_4\text{O}_2\text{P}^+$) are observed with high intensity (100% and 71%, respectively).

2.1.1.1 Spectroscopic Data

NMR data of the compounds 2.1 and 2.2 are listed in Tables 10-12.

Table 10: ^{11}B - and ^{31}P -NMR Data of the Products 2.1-2.4 (in ppm; half-widths in Hz; solvents numbered as in Table 1)

<u>Nr.</u>	<u>$\delta^{11}\text{B}$</u>	<u>$h_{1/2}$</u>	<u>$\delta^{31}\text{P}$</u>	<u>Solvent</u>	<u>$\delta^{31}\text{P}$ (S.M.)^a</u>
<u>2.1</u>	45.7	940	193	1	173
<u>2.2</u>	46.0	780	193	2	196
<u>2.3</u>	46.4	680	188	2	169
<u>2.4</u>	45.9	780	185	1	175 ^b

a. Lit.: 7

b. See Experiment 2.4.

Table 11: ^1H -NMR Data of the Products 2.1-2.4 (in ppm; solvents as in Table 10)

<u>Nr.</u>	<u>CH_3</u> (tmp)	<u>CH_2</u> (tmp)	<u>arom.H</u> (fluorene)	<u>other</u>
<u>2.1</u>	1.10	1.51-1.56	6.98-7.40(4H) 7.62-7.89(4H)	6.43-6.70(4H) (phenyl)
<u>2.2</u>	1.20	1.28-1.65	7.02-7.38(4H) 7.77-8.11(4H)	6.55(4H)
<u>2.3</u>	0.83	0.87-1.29	6.85-7.12(4H) 7.47-7.58(2H) 7.72-7.82(2H)	2.30-2.70(4H) (CH_2CH_2)
<u>2.4</u>	1.29	1.32-1.75 ^a	6.98-7.77	a

a. tmp- CH_2 and $(\text{CH}_3)_2\text{C}_2\text{O}_2\text{P}$ fall together. Integral = 18H.

Table 12: ^{13}C -NMR Data of the Products 2.1-2.4 (in ppm; solvents as in Table 11; numbering scheme as in Fig. 1.1; $^{\text{N}}\text{J}(^{31}\text{P}-^{13}\text{C})$ values in brackets, given in Hz)

Table 12a: ^{13}C -Resonances of the tmp ring

<u>Nr.</u>	<u>C4</u>	<u>C7/8</u>	<u>C3/5</u>	<u>C2/6</u>	<u>other</u>
<u>2.1</u>	15.6	32.4	37.4	57.6	a
<u>2.2</u>	16.1	32.2	37.9	57.8	b
<u>2.3</u>	16.1	32.2	37.7	57.0	c
<u>2.4</u>	16.0	32.2	37.7	57.1	d

Table 12b: ^{13}C -Resonances of the fluorene ring

<u>Nr.</u>	<u>C9</u>	<u>C10</u>	<u>C15</u>	<u>C11</u>	<u>C12</u>	<u>C13</u>	<u>C14</u>
<u>2.1</u>	n.o.	141.3	141.3	122.1	126.3	127.0	120.2
<u>2.2</u>	76.5 (35)	141.4	141.3	122.2	126.5	126.7	120.3
<u>2.3</u>	n.o.	144.4 (2)	141.2	126.1 (5)	126.4	126.7	120.6
<u>2.4</u>	n.o.	144.5 (6)	141.4	126.1	126.4	126.4	120.3

n.o. = not observed owing to signal broadening (boron-bound C-atom).

a. 148.0, 127.0, 111.6 (phenyl)

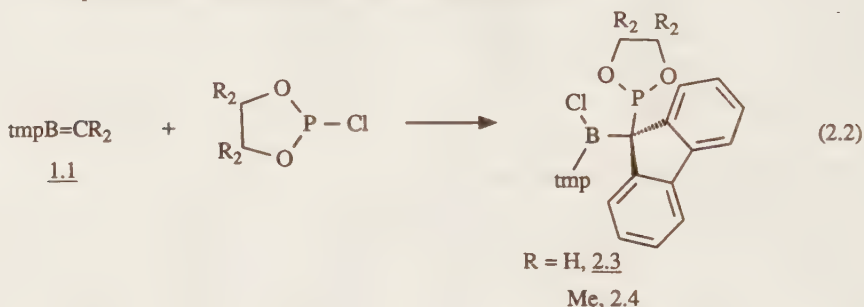
b. 148.2, 127.1, 111.7 (phenyl)
(7)

c. 66.1 ($-\text{OCH}_2\text{CH}_2\text{O}-$)
(10)

d. 24.5, 25.8 ($\text{O}_2\text{C}_2(\text{CH}_3)_4$), 83.8 ($\text{O}_2\text{C}_2(\text{CH}_3)_4$)
(5)

2.1.2 Reaction with 2-Chloro-1,3,2-dioxaphospholanes

$\text{tmpB}=\text{CR}_2$ and 2-chloro-1,3,2-dioxaphospholane react rapidly at room temperature in toluene to yield the product 2.3 (eq. 2.2).



Reaction was found to be complete by ^{11}B -NMR and ^{31}P -NMR after 2h. The product 2.3 was not as easy to isolate as 2.1 and 2.2, requiring that only a small amount of hexane be used, followed by several days standing at -20°C . The yield was correspondingly low, and the product is much more sensitive towards moisture and air. 2.3 was fully characterized by analysis and NMR. NMR data are listed in Tables 10-12 (see above, section 2.1.1).

The ^{11}B -NMR signal at $\delta^{11}\text{B} = 46.4$ ppm is very similar to those found for 2.1 and 2.2, and thus corresponds to a bulky (*via* C9-substitution) chloro(organyl)(tmp)borane.

The ^{31}P -NMR signal of 2.3 at 188.0 ppm lies downfield from the starting material⁷⁾, the difference being $\Delta\delta^{31}\text{P} = 19.0$ ppm. This is in good agreement with $\Delta\delta^{31}\text{P}$ found for 2.1.

The ^1H -NMR spectrum of 2.3 indicates a significant high-field shift for both the tmp methyl protons ($\delta^1\text{H} = 0.83$ ppm) and the methylene protons of the dioxaphospholano unit. The latter are found at $\delta^1\text{H} = 2.30\text{--}2.70$ ppm in 2.3. In $\text{tmpB}(\text{OMe})\text{N}^i\text{Bu}(\text{P}(\text{OCH}_2\text{CH}_2\text{O}))^1$, the methylene protons of the dioxaphospholano unit are found at $\delta^1\text{H} = 3.85$ ppm. The large high-field shift in 2.3 can be explained by the anisotropic shielding effect of the fluorenyl ligand.

The magnitude of the shift results from the proximity of the dioxaphospholano moiety to the fluorenyl ring system.

The ^{13}C -NMR spectrum of 2.3 indicates that the symmetry at phosphorous (ie. no chiral center) is preserved and hence only one set of signals for the fluorene moiety is found. The electronic and steric environment in 2.3, though similar to 2.1 and 2.2, is slightly different, being reflected in a visible $^3\text{J}(^{31}\text{P}-^{13}\text{C})$ to C11 of 5 Hz. This is comparable to ^3J found for C11 in many of the compounds described in Chapter 1 (see Chapter 1, Table 3b). The $^2\text{J}(^{31}\text{P}-^{13}\text{C})$ value of 2 Hz for C10 is also comparable to coupling constants as observed in similar compounds. The ethylene unit from the dioxaphospholano group has a ^{13}C -NMR signal at $\delta^{13}\text{C} = 66.1$ ppm with $^2\text{J}(^{31}\text{P}-^{13}\text{C}) = 10$ Hz. The ^{13}C -NMR shift and ^2J coupling constant represent almost no change compared to the starting material ($\delta^{13}\text{C} = 65.3$ ppm; $^2\text{J} = 9$ Hz)⁸.

As described in Chapter 1, several substituted phosphorous(III) halides failed to react with $\text{tmpB}=\text{CR}_2$, in spite of long reaction times (tmpPCl_2), harsh conditions ($^t\text{BuPCl}_2$), and adequate Lewis acidity. The reasons for lack of reaction were assumed to be steric. It was thus of interest to continue to attempt reactions between $\text{tmpB}=\text{CR}_2$ and sterically hindered, but otherwise reactive, compounds, in the hope of finding examples which clearly demonstrate that the reactions can succeed, however slowly. Finding such an example would imply that the system had been pushed to its steric limits ($^t\text{BuPCl}_2$ and tmpPCl_2 both clearly being beyond these limits).

2-chloro-1,3,2-tetramethyldioxaphospholane⁹) reacts with $\text{tmpB}=\text{CR}_2$ (according to eq. 2.2) over a period of 3 weeks at room temperature in toluene to give 2.4. 2.4 can be isolated from hexane at -20°C as a fairly stable, crystalline compound, whose composition and structure were determined by analysis and NMR. NMR data are listed in Tables 10-12 (see above, section 2.1.1).

The ^{11}B -NMR signal at 45.9 ppm represents almost no change from the series 2.1-2.4. Likewise, the ^{31}P -NMR signal at $\delta^{31}\text{P} = 185.0$ ppm is similar to the signals found for 2.1-2.3 ($\delta^{31}\text{P} = 188.0$ ppm - 192.8 ppm).

The ^1H -NMR spectrum of 2.4 is more difficult to interpret because the methyl groups from the pinacole unit and the methylene protons of tmp fall within

a small region, and exact assignment is not possible ($\delta^1\text{H} = 1.32\text{-}1.75$ ppm, $I = 18\text{H}$, for 6 tmp methylene protons and 12 pinacole protons).

The ^{13}C -NMR spectrum of 2.4 is very similar to those of 2.1-2.3, with no coupling observed between C11 and P. However, a large 2J value is found for C10 ($^2J = 6$ Hz), though this value is certainly within bounds for $^2J(^{31}\text{P}\text{-}^{13}\text{C})$. (Compare compound 1.3, $^2J(^{31}\text{P}\text{-}^{13}\text{C}10) = 8$ Hz, section 1.2.1.) The oxygen-bound carbon atoms are found at $\delta^{13}\text{C} = 83.8$ ppm ($^2J(^{31}\text{P}\text{-O-}^{13}\text{C}) = 5$ Hz), and this agrees well with the data obtained for the starting material ($\delta^{13}\text{C} = 88.8$ ppm, $^2J = 8$ Hz). The methyl groups of the pinacole unit are split, being observed at $\delta^{13}\text{C} = 24.5$ and 25.8 ppm, only the latter showing a coupling to ^{31}P : $^3J(^{31}\text{P}\text{-O-}^{13}\text{C-}^{13}\text{C}) = 5\text{Hz}$. In the starting material, a similar splitting of the ^{13}C -NMR signals is observed ($\delta^{13}\text{C} = 24.6$ ppm and 25.4 ppm, with the latter signal coupling to phosphorous: $^3J = 3.5$ Hz). These results can be explained by considering that phosphorous possesses a stereochemically active lone pair which, as is demonstrated in Fig. 2.1, can interact more strongly with the methyl groups situated *cis* to it. This argument can be used to explain both the different chemical shifts and coupling constants found in the starting material and product.

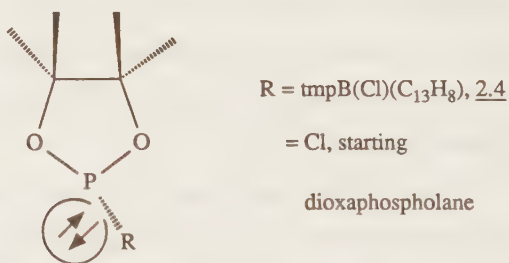
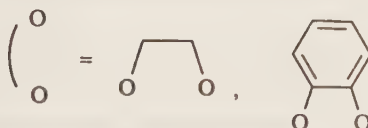


Fig. 2.1: Perspective drawing of P-substituted 1,3,2-tetramethyldioxaphospholanes showing the stereochemically active lone pair.

With the synthesis of 2.1-2.4, a very important difference between the reactivities of $\text{tmpB}\equiv\text{N}^t\text{Bu}$ and $\text{tmpB}=\text{CR}_2$ has been uncovered. In all cases, 2.1-2.4, the halogen atom was transferred from phosphorous to boron. For the amino-imino-borane, $\text{tmpB}\equiv\text{N}^t\text{Bu}$, the opposite was found to be the case, as shown in eq. 2.3:



Thus, a seven-membered ring was obtained, regardless of the dioxo-ring or the halogen substituent used¹⁾. This points to an important difference between the two systems: the presence of the imino-N atom in tmpB≡N^tBu allows for an initial nucleophilic attack of N at phosphorous, which thereby labilizes the P-O bond. tmpB=CR₂ lacks a strongly nucleophilic center. Reactions most likely proceed (in contrast to tmpB≡N^tBu) *via* electrophilic attack of the boron atom at a fairly labile center. In the reactions leading to 2.1-2.4, the P-Cl or P-Br bond is the most labile and is, therefore, the bond broken in the reactions.

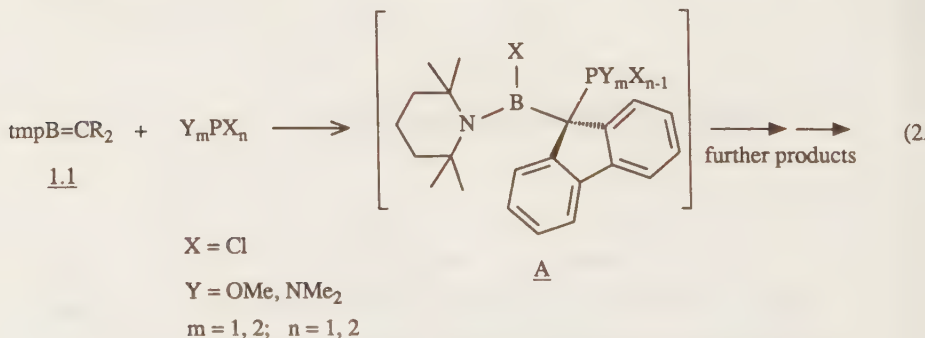
2.1.3 Reaction with 2-Methoxy-1,3,2-dioxaphospholane

Stirring equimolar amounts of tmpB=CR₂ and 2-methoxy-1,3,2-dioxaphospholane at room temperature in toluene for several weeks resulted in no reaction. Only a small amount of hydrolysis or oxidation product could be detected in the ¹¹B-NMR spectrum (δ¹¹B = 59.0 ppm; δ¹¹B = 36.9 ppm, ca 15%). The ³¹P-NMR spectrum indicated no change whatsoever (δ³¹P = 132.0 ppm). This is in marked contrast to the reactivity of tmpB≡N^tBu, though it is consistent with the failure of P(OMe)₃ to react with tmpB=CR₂ (section 1.2.2). Interestingly, tmpB≡N^tBu also did not react with P(OMe)₃ but nonetheless reacted

with the cyclic compound 2-methoxy-1,3,2-benzodioxaphospholane, not to give the seven-membered heterocycle, but with transfer of a methoxy group¹⁾. The reasons for these subtle differences in reactivity patterns are not clear.

2.1.4 Reaction with 2-Fluoro-1,3,2-benzodioxaphospholane

$\text{tmpB}=\text{CR}_2$ and 2-fluoro-1,3,2-benzodioxaphospholane fail to react at room temperature. Heating the mixture does not induce addition. The reason for this failure to react is most likely the strenghts of the P-F and P-O bonds. As discussed earlier (see chapter 1), their labilization *via* electrophilic attack appears to be a necessary criterion for reaction with $\text{tmpB}=\text{CR}_2$. This further implies that the reactions in Chapter 1 which failed to yield stable addition products (e.g. $\text{P(OMe)}_2\text{Cl}$, $\text{P(NMe}_2)_2\text{Cl}$) most likely proceed *via* the addition product A, obtained from halogen-atom transfer. From A, the decomposition products arise (eq. 2.4).

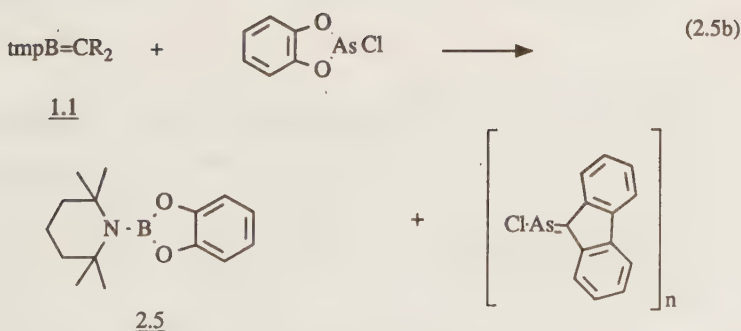
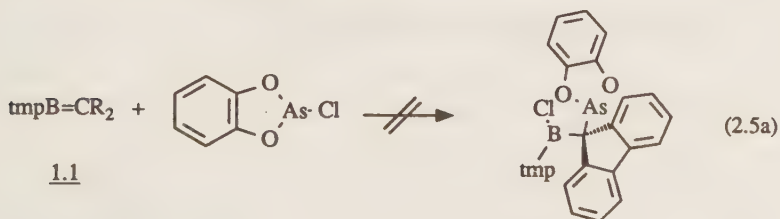


Only in the case of $\text{P(NMe}_2)_2\text{Cl}_2$ could the product A be isolated. The reason for the instability of the other products is not certain.

2.2 Reactions of $\text{tmpB}=\text{CR}_2$ with Cyclic Arsenic(III) and Antimony(III) Compounds

2.2.1 Reaction with 2-Chloro-1,3,2 -benzodioxarsolane

Because of the unusual stability of the halogeno-dioxaphospholane adducts, 2.1-2.4, it was hoped that the corresponding As(III) and Sb(III) compounds would similarly yield stable products. $\text{tmpB}=\text{CR}_2$ and 2-chloro-1,3,2-benzodioxarsolane in toluene at room temperature do not yield an addition product but rather the known compound 2.5, and the corresponding chloro-fluorenylidene-arsane (eq. 2.5a,b).

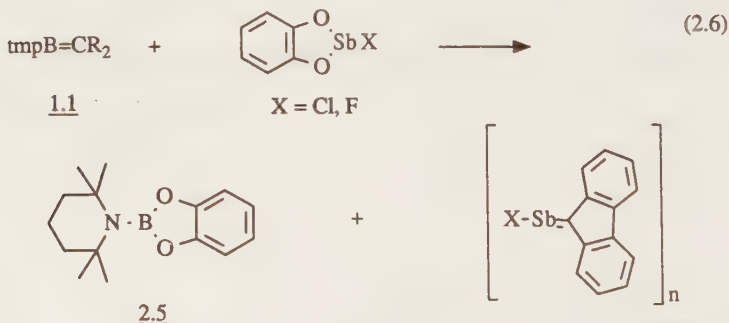


Though 2.5 could not be isolated cleanly, it was readily characterized by its ^{11}B - and ^1H -NMR spectra ($\delta^{11}\text{B} = 26.7$ ppm; $h_{1/2} = 210$ Hz; Lit: $\delta^{11}\text{B} = 26.7$ ppm; $h_{1/2} = 200$ Hz¹⁾). Along with 2.5, traces of a fluorene-containing product were also detected by ^1H -NMR ($\delta^1\text{H} = 6.86\text{-}7.65$ ppm). The nature of this product could not,

however, be determined. The only indication that it could be a fluorenylidene-arsane fragment was the bright orange-yellow color of the solid material isolated.

2.2.2 Reaction with 2-Halogeno-1,3,2-benzodioxastibolane

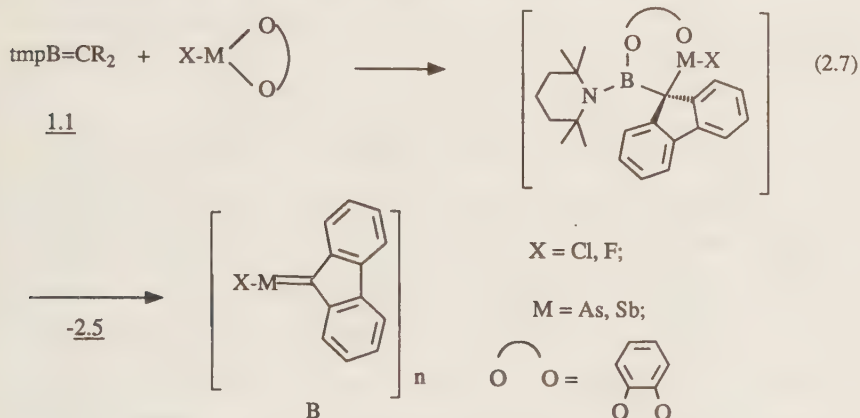
Stirring $\text{tmpB}=\text{CR}_2$ and 2-fluoro- or 2-chloro-1,3,2-benzodioxastibolane in toluene for several hours at room temperature fails to yield the simple addition products, but rather the compound 2.5, along with the corresponding fluorenylidene-halogeno-stibanes (equation 2.6).



The formation of 2.5 could be demonstrated only by its ^{11}B -NMR spectrum ($\delta^{11}\text{B} = 26.4$ ppm, $h_{1/2} = 170$ Hz; and $\delta^{11}\text{B} = 26.8$ ppm, $h_{1/2} = 220$ Hz; for $\text{X} = \text{F}$ and Cl , respectively). All attempts to isolate a spectroscopically clean product (either 2.5 or one of the stibanes) by crystallization at low temperature resulted in failure.

These results with 2-halogeno-1,3,2-dioxaarsolane and -stibolane contrast to those presented in the first part of this chapter with 2-halogeno-1,3,2-dioxaphospholanes. As was discussed earlier, the lability of the metal-halogen or metal-oxygen bonds (metal = P, As, Sb) is most likely the decisive factor in determining the reaction paths. With phosphorous it was shown

that only the P-halogen bond is labile enough to react with the electrophilic B=C center. In the cases of As and Sb, it was known from Chapter 1 that the trihalides can react. From these latest examples it is clear that the As-O and Sb-O bonds are also labile with respect to the B=C unit. A reaction path involving a cyclic intermediate B can be imagined for these latter reactions (eq. 2.7).

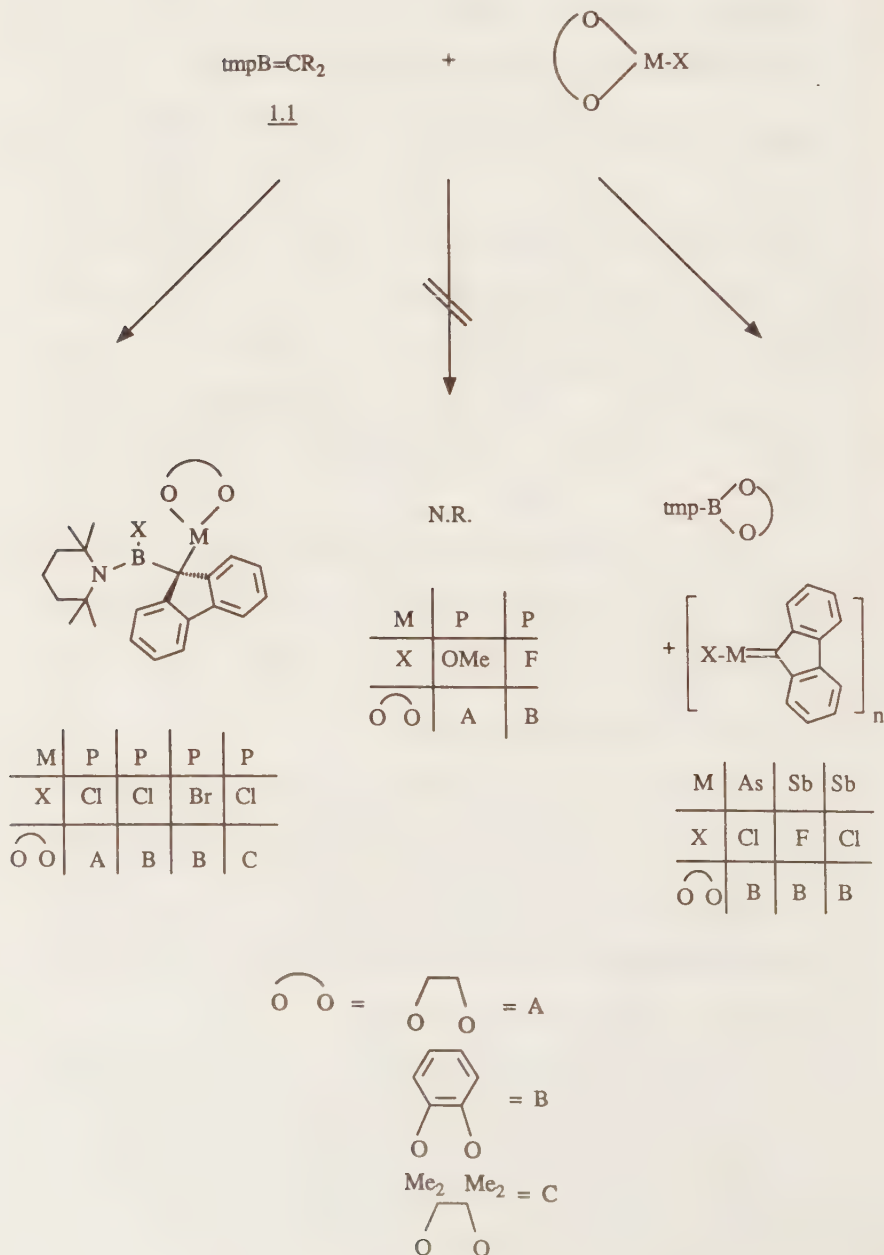


Because of a) the availability of two labile metal-oxygen bonds in the starting dioxarsolanes and -stibolanes and b) the well-known inherent stability of BO_2C_2 -five-membered heterocycles such as 2.5, B then breaks down to yield the products 2.5 and, most likely, some oligomeric form(s) of the fluorenylidene-halogeno-arsanes and -stibanes.

This reactivity pattern is furthermore consistent with the reactivity of $\text{tmpB}\equiv\text{N}^t\text{Bu}$ which also reacts with the 2-chloro-1,3,2-benzodioxarsolanes and -stibolanes to yield 2.5 and the corresponding (dimeric) chloro-imino-arsananes and stibananes¹⁾. The use of bulky amine substituents or alkyl or aryl groups at As and Sb could lead to stable As- and Sb-fluorenylidene complexes. Work in this area is currently being pursued in our laboratories¹⁰⁾.

In summary, depending on the metal and the nature of the substituents at the metal, tmpB=CR_2 reacts to stable addition products, to products arising from the rupture of both boron-carbon bonds, or it fails to react altogether (Fig. 2.2).

Fig 2.2: Summary of reactivity patterns of $\text{tmpB}=\text{CR}_2$ towards cyclic P(III), As(III), and Sb(III) halides.



Chapter 3:

Reactions of $\text{tmpB}=\text{CR}_2$ with Halides of the Main Group IV Elements and with Halides and Related Complexes of Titanium(IV) and Hafnium(IV)

3.1 Introduction

Up to this point, the reactivity of the amino-fluorenylidene-borane 1.1 has been discussed largely in terms of its Lewis-acidic character and its tendency to form 1:1 insertion products with various metal halides. These can all be aptly described as boryl-substituted alkyl compounds, in which the fluorenyl ligand has played the role of the alkyl substituent. Because of this fact, analogy has been drawn between the reactivity of $\text{tmpB}=\text{CR}_2$ and $\text{tmpB}\equiv\text{N}^t\text{Bu}$, the former yielding alkyl-functionalized, the latter amino-functionalized boranes. In this chapter, the reactivity of Si, Sn, and Ge tetrahalides as well as compounds of Ti(IV) and Hf(IV) towards $\text{tmpB}=\text{CR}_2$ will be discussed.

Before discussing the results obtained, a brief summary of the chemistry of the fluorenyl ligand will be presented, to place these results in historical perspective.

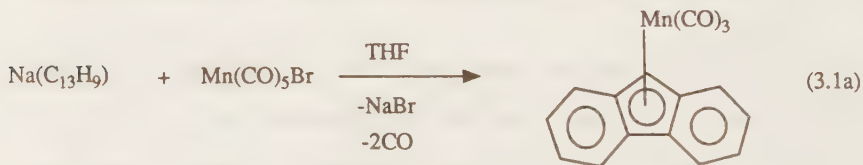
In 1953, shortly after the discovery of ferrocene by Kealy and Pauson¹⁾, many attempts were made to extend this chemistry both to different metals (eg. Ru, Co, Ni)²⁾ and to various substituted cyclopentadienyl ligands. Pauson and Wilkinson were able to synthesize the bis(η^5 -indenyl)-complexes of both iron and cobalt³⁾, but found them to be rather unstable relative to their cyclopentadienyl analogues. This lack of stability led Pauson to comment in an early review article⁴⁾, that it was, therefore, not surprising that the corresponding bis(fluorenyl)-compounds had continued to elude the early metallocene chemists. In 1955, Weinmayr successfully synthesized an octaphenyl-ferrocene derivative, and thereby destroyed any arguments based on steric restraints of the fluorenyl ligand. This led Pauson and others to conclude that the fluorenyl ligand was

simply an exception, most likely for electronic reasons, and that further attempts to synthesize (η -fluorenyl)-complexes would prove to be futile^{4),5)}.

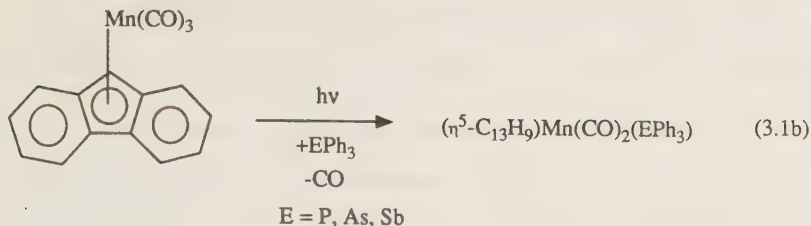
Indeed, it was not until 1960 that Fischer and Kriebitzsch successfully synthesized the first π -complex of fluorene, in analogy to (η^6 -benzene) $\text{Cr}(\text{CO})_3$ and (η^6 -indene) $\text{Cr}(\text{CO})_3$ ⁶⁾. In the paper reporting this first example of a fluorene-transition metal complex, the authors also mentioned (like Pauson and Wilkinson before them) their unsuccessful attempts to synthesize the ferrocene analogues of the fluorenyl ligand.

Five years later, Samuel and Setton published a report of the syntheses of (η^5 -indenyl) $_2\text{ZrCl}_2$, (η^5 -indenyl) $_2\text{TiCl}_2$, and the corresponding (η^5 -fluorenyl) derivatives in analogy to the well-known Cp_2MCl_2 compounds ($\text{M} = \text{Zr}, \text{Ti}$)⁷⁾. However, the compounds were found to be very unstable, especially in the cases of the fluorenyl derivatives, and could only be characterized by analysis and I.R. Attempts to synthesize (η^5 -fluorenyl) $_2\text{TiCl}_2$ led to a solid product, but its metal content could not be determined.

It was not until 1970, nearly twenty years after the discovery of the metallocenes, that the first (η^5 -fluorenyl)-transition metal complex was synthesized. King and Efraty⁸⁾ found that reaction of $\text{Na}(\text{C}_{13}\text{H}_9)$ in THF with $\text{Mn}(\text{CO})_5\text{Br}$ yielded (η^5 -fluorenyl) $\text{Mn}(\text{CO})_3$ in poor yield (eq. 3.1a).

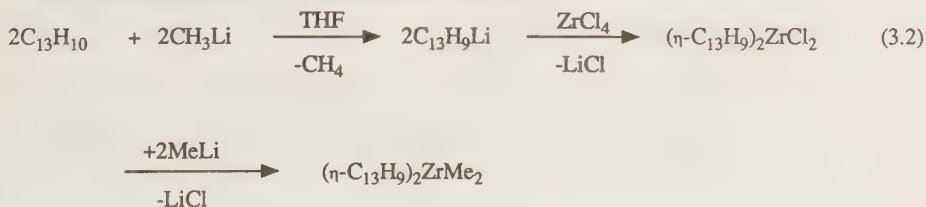


Photolytic substitution reactions produced the mono-substituted derivatives (η^5 -fluorenyl) $\text{Mn}(\text{CO})_2(\text{EPh}_3)$ ($\text{E} = \text{P}, \text{As}, \text{Sb}$) (eq. 3.1b).



Following this report of the first unequivocal example of a complex containing a η^5 -fluorenyl ligand, interest in the field took hold again. In 1971, Nicholas, *et al.* reported the deprotonation reaction of the Fischer-fluorene complex $(\eta^6\text{-C}_{13}\text{H}_{10})\text{Cr(CO)}_3$ to yield the anion $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr(CO)}_3\text{K}^+$ which could be characterized by its $^1\text{H-NMR}$ spectrum but not isolated⁹). This was followed in 1974 by the report of the crystal structure of $(\eta\text{-fluorenyl})_2\text{ZrCl}_2$, which proved to contain one η^3 - and one η^5 -fluorenyl ligand¹⁰) and thereby provided the first example of η^3 -(π -allylic)-bonding of a planar π -bonded ring to a metal center. It also added some interest to a debate sparked by Cotton in which he had refuted the likelihood of trihapto bonding of cyclopentadienyl rings¹¹).

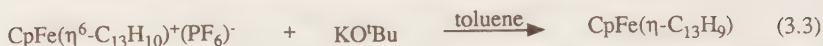
This study led Samuel, *et al.* to reinvestigate the bis(fluorenyl) ZrCl_2 system and they found that the one-pot reaction of fluorene, methyl lithium, and ZrCl_4 in THF led to high yields of $(\eta^5\text{-fluorenyl})_2\text{ZrMe}_2$ (eq. 3.2).



The product could be well characterized and was found to contain photolytically labile methyl groups¹²).

In spite of this activity, however, the ferrocene analogue, $(\eta^5\text{-C}_{13}\text{H}_9)_2\text{Fe}$, remained elusive. Then, in 1976 Treichel and Johnson used an elegant method to synthesize $\text{CpFe}(\eta\text{-C}_{13}\text{H}_9)$ from the previously known¹³) ionic species

$\text{CpFe}(\text{C}_{13}\text{H}_{10})^+\text{PF}_6^-$ and potassium tert-butoxide in toluene (eq. 3.3)¹⁴.



Drawing analogy between their system and $(\eta^5\text{-fluorenyl})\text{Cr}(\text{CO})_3 \cdot \text{K}^+$, they assumed they had obtained the expected $\eta^6 \rightarrow \eta^5$ migration. However, the crystal structure of $\text{CpFe}(\eta\text{-C}_{13}\text{H}_9)$ indicated the maintenance of η^6 -coordination¹⁴. They explained this phenomenon by assuming a zwitterionic structure (Fig. 3.1).

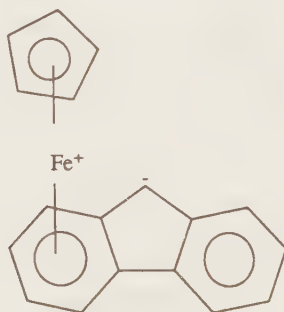
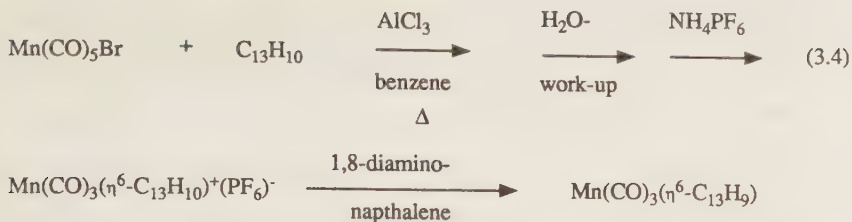


Fig. 3.1

The difference between the coordination in their system and in King's $(\eta^5\text{-fluorenyl})\text{Mn}(\text{CO})_3$ lay in the **metal's ability to withdraw electron density from the ligand**. In $(\eta^5\text{-fluorenyl})\text{Mn}(\text{CO})_3$, the CO ligands, being good π -acceptors, increase the metal's ability to withdraw electron density from the fluorenyl ligand. Cp, being a much weaker π -acceptor than CO, resulted in the unexpected structure found. The same argument would presumably hold for $(\eta\text{-fluorenyl})_2\text{ZrCl}_2$ because of the two electronegative chlorine substituents at the Zr-center.

Knowing beforehand that $(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$ was a stable, isolable complex, Johnson and Treichel then applied a methodology similar to that used for $\text{CpFe}(\eta^6\text{-C}_{13}\text{H}_9)$ to the synthesis of the new complex $(\eta^6\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$ as a kinetically stable product (eq. 3.4)¹⁵.

This compound was characterized by NMR and X-ray crystallography.



Furthermore, it was demonstrated that refluxing the compound in hexane for one hour resulted in irreversible migration of Mn(CO)_3 to the center ring ($\eta^6 \rightarrow \eta^5$).

Since that time, $(\eta^5\text{-fluorenyl})\text{Mn(CO)}_3$ has found extensive use by Basolo and co-workers in their studies of the mechanism of associative ligand-substitution reactions at $(\eta\text{-cyclopentadienyl})\text{metal carbonyl centers}$ ^{16,17}. The results of their studies will prove to be important in light of results obtained in this work (see below, section 3.5).

Thus, at the start of this work, few transition metal-fluorene complexes had been isolated, and only four had been characterized by X-ray crystallography.

This work, as will be seen in this chapter, has added 3 examples of η^3 - or η^5 -coordinated fluorene complexes and several examples of a completely new type of coordination, which, because of its extreme novelty, will be discussed separately (see chapter 5). Fluorene, as a complex ligand, seems finally to have come into its own...*via* main group chemistry.

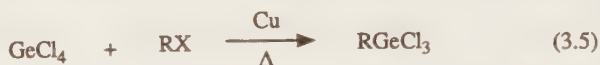
3.2 Reactions with Halides of Main Group IV

U. Strobl¹⁸⁾ reported that SiCl_4 does not react with tmpB=CR_2 to yield the expected addition product and concluded that the Si-Cl bond is simply too strong for reaction to occur. This is in contrast to the result found for $\text{tmpB}\equiv\text{N}^t\text{Bu}$ ¹⁹⁾, which reacts with SiCl_4 , even at low temperature. As was discussed in Chapter 2, however, $\text{tmpB}\equiv\text{N}^t\text{Bu}$ seems in general to be able to labilize bonds *via* an initial nucleophilic attack of the imino-N at an electrophilic metal center. tmpB=CR_2 ,

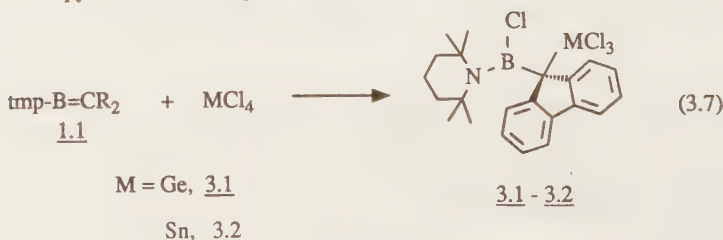
being a much weaker nucleophile, is therefore more dependent on weaker, more labile metal-ligand bonds in order for an addition reaction to occur. Because GeCl_4 and SnCl_4 are known to contain more labile M-Cl bonds²⁰, their reactions with $\text{tmpB}=\text{CR}_2$ were to be studied.

3.2.1 Reaction with Germanium Tetrachloride

Based on the 35 kJ/mol weaker metal-chloride bond in GeCl_4 than in SiCl_4 , it was hoped that the addition reaction to yield the (chloro(tmp)boryl)fluorenyl trichlorgermane would prove successful. Mono-alkyl germanium trihalides are generally prepared from GeCl_4 and alkyl halides in the presence of copper catalysts (eq. 3.5)²¹ or by the oxidative addition reaction between RX and Ge(II) halides (eq. 3.6)²².



Indeed $\text{tmpB}=\text{CR}_2$ reacts smoothly with GeCl_4 in toluene at 25°C to yield the 1:1 addition product, 3.1 (eq. 3.7). The product is a stable, colorless, crystalline solid, which could be readily characterized by analysis, NMR and mass spectroscopy. NMR data are given in Tables 13-15.



The mass spectrum of 3.1 contains the parent ion with 100% intensity at

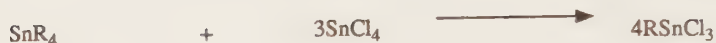
$m/e = 529$ (^{11}B , ^{35}Cl , ^{74}Ge) with the correct calculated isotope pattern. In addition to the 100% fragment at $m/e = 529$, other typical intense fragments for tmp, fluorene and M-GeCl_4 are found. The second most intense is that at $m/e = 350$, $(\text{M-GeCl}_3)^+$.

The ^{11}B -NMR spectrum of 3.1 indicates the presence of a chloro(organyl)(tmp)borane. The signal at $\delta^{11}\text{B} = 42.4$ ppm ($h_{1/2} = 470$ Hz) indicates almost exactly the same shielding as that found for the PCl_3 adduct, 1.2. The ^1H -NMR spectrum does not differ drastically from those found for non-substituted metal-halide adducts of P, As and Sb (see Chapter 1). However, the shielding effect from the fluorenyl ring system is even stronger than for the M(III)X_3 adducts (for tmp methyl protons in 3.1, $\delta^1\text{H} = 0.77$ ppm). This is understandable since there are now three Cl-atoms on the metal center bound to C9. This would be expected to have the effect of forcing the tmp and fluorenyl substituents closer together. The methylene protons in tmp ($\delta^1\text{H} = 1.33$ ppm) are also found at higher field.

The ^{13}C -NMR spectrum of 3.1 has no outstanding features except that it indicates a symmetric environment at C9: only one set of six ^{13}C -NMR signals is found for fluorene and four for tmp. The two quaternary C-atoms in fluorene are found at $\delta^{13}\text{C} = 140.2$ and 141.3 ppm (C15 and C10, respectively), and thus no significant carbon-metal interaction is indicated.

3.2.2 Reaction with Tin Tetrachloride

As opposed to their germanium analogues, mono-alkyl tin trihalides do not tend to be very stable, readily undergoing base-catalyzed redistribution reactions to both di- and tri-alkyl Sn(IV) halides²⁵. In practice, the redistribution reaction is taken advantage of in the synthesis of mono-alkyl Sn(IV) halides. First, the tetraalkyl tin is made from SnCl_4 and the Grignard reagent, followed by redistribution to the desired product (eq. 3.8)²³⁻²⁵.



As in the case of the GeCl_4 adduct, 3.1, it was hoped that $\text{tmpB}=\text{CR}_2$ would react with SnCl_4 to yield a 1:1 adduct and, for steric reasons, fail to undergo the further reaction to the dialkyl tin dichloride.

This proved to be the case. $\text{tmpB}=\text{CR}_2$ and SnCl_4 react rapidly at room temperature in toluene to yield the product 3.2 (eq. 3.7), as stable lemon-yellow crystals, sensitive only to heat (warming toluene solutions results in metal deposition).

The mass spectrum of 3.2 does not contain the parent ion at $m/e = 575$ (^{11}B , ^{35}Cl , ^{119}Sn) but the fragment $(\text{M-tmp})^+$ at $m/e = 435$ with 5 % intensity.

The correct isotope pattern is found. The most intense peak (as with most of the insertion products of the main group V halides) is found at $m/e = 350$ for the $(\text{M-SnCl}_3)^+$ fragment.

The ^{11}B -NMR spectrum of 3.2 ($\delta^{11}\text{B} = 41.3$ ppm) indicates the presence of a chloro(organyl)(tmp)borane, and the shielding differs only slightly from that in the GeCl_4 adduct, 3.1. Thus, 3.1 and 3.2 are found in regions very similar to the P, As, and Sb trihalide adducts, implying very similar electronic and steric environments. This is further supported by the ^1H - and ^{13}C -NMR spectra of 3.2, as well as its ^{119}Sn -NMR spectrum (Tables 13-15, see below).

The ^{119}Sn -NMR shift at $\delta^{119}\text{Sn} = -177$ ppm is upfield from the region of other mono-alkyl tin trichlorides (MeSnCl_3 , $\delta^{119}\text{Sn} = 20$ ppm; PhSnCl_3 , $\delta^{119}\text{Sn} = -63$ ppm). However, much greater differences are usually found between 4- and 5-coordinate tin compounds²⁵⁾⁻²⁶⁾. Nonetheless, the shielding of 3.2 relative to other mono-alkyl tin trichlorides could imply a slight amount of interaction between the boron-bound Cl-atom and the Sn-atom.

The ^1H -NMR spectrum of 3.2 further supports the idea that a MCl_3

fragment at C9 (as opposed to MCl_2 fragments in the analogous P, As, and Sb compounds) results in the tmp ring and the fluorenyl ligand being pushed closer together. This has the effect of greater anisotropic shielding of both the methyl ($\delta^1\text{H} = 0.77$ ppm) and the methylene ($\delta^1\text{H} = 1.32$ ppm) protons of tmp.

Likewise, the ^{13}C -NMR spectra of 3.1 and 3.2 are nearly identical. The major difference is that $^n\text{J}(^{119}\text{Sn}-^{13}\text{C})$ couplings are observed for C11-C14 ($n = 3, 4, 5$) in 3.2. These couplings lie between 15.4 and 26.4 Hz, acceptable values for ^3J but large for ^4J and ^5J . However, the ^{119}Sn - ^{13}C interaction has been shown to be strongly dependent, in a Karplus-type relationship, on the dihedral angle. Taking this into consideration, compounds have been found with ^3J as large as 69.0 Hz²⁸.

Furthermore, coupling through four bonds has been observed in Ph_3SnCl ($^4\text{J} = 12$ Hz) and Ph_2SnCl_2 ($^4\text{J} = 16$ Hz)²⁹. That a mesomeric effect is at work in our system is certainly possible. This would explain the observable ^4J and ^5J values. (Tables 13, 14, 15: ^{11}B -, ^{119}Sn -, ^1H - and ^{13}C -NMR Data).

Table 13: ^{11}B - and ^{119}Sn -NMR Data of the Products 3.1 and 3.2 (in ppm; half-widths in Hz; solvents numbered as in Table 1)

<u>Add of.</u>	<u>Nr.</u>	<u>$\delta^{11}\text{B}$</u>	<u>$h_{1/2}$</u>	<u>$\delta^{119}\text{Sn}$</u>	<u>Solvent</u>
GeCl_4	<u>3.1</u>	42.4	470	---	1
SnCl_4	<u>3.2</u>	41.3	480	-177	2

Table 14: ^1H -NMR Data of the Products 3.1 and 3.2 (in ppm; solvents as in Table 13)

<u>Add. of</u>	<u>Nr.</u>	<u>CH₃</u> (tmp)	<u>CH₂</u> (tmp)	<u>arom. H</u> (fluorene)
GeCl ₄	<u>3.1</u>	0.77	1.33	7.20-7.40(4H) 7.63-7.82(4H)
SnCl ₄	<u>3.2</u>	0.77	1.32	7.11-7.32(4H) 7.61-7.77(4H)

Table 15: ^{13}C -NMR Data of the Products 3.1 and 3.2 (in ppm; solvents as in Table 13; numbering scheme as in Fig. 1.1; $^n\text{J}(^{119}\text{Sn}-^{13}\text{C})$ values in brackets, given in Hz)

Table 15a: ^{13}C -Resonances of the tmp ring

<u>Nr.</u>	<u>C4</u>	<u>C7/8</u>	<u>C3/5</u>	<u>C2/6</u>
<u>3.1</u>	14.5	31.9	36.3	57.9
<u>3.2</u>	14.2	31.8	35.8	58.5

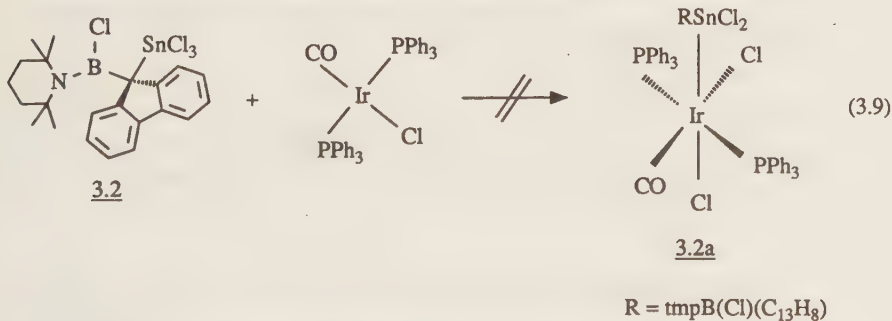
Table 15b: ^{13}C -Resonances of the fluorene ring

<u>Nr.</u>	<u>C9</u>	<u>C10</u>	<u>C15</u>	<u>C11</u>	<u>C12</u>	<u>C13</u>	<u>C14</u>
<u>3.1</u>	n.o.	141.3	140.2	126.7	127.5	128.4	120.7
<u>3.2</u>	n.o.	139.8	139.8	125.3	127.8	128.3	121.1
		(21)		(26)	(21)	(21)	(15)

n.o. = not observed owing to signal broadening; boron-bound C-atom.

3.2.2.1 Reaction of 3.2 with Vaska's Complex, $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$

The discovery of Vaska's complex³⁰⁾ is often heralded as one of the great turning points in organometallic chemistry, demonstrating for the first time the full scope and potential of the oxidative addition reaction³¹⁾. Among the reactions which the Vaska complex has been found to undergo are the reactions with SnCl_4 , R_3SnCl ($\text{R} = \text{Me}$) and Ph_2SnCl_2 ³²⁾. It was hoped that, viewing 3.2 as a monoalkyl-SnCl₃ species, reaction would proceed as in eq. 3.9.



However, combining the two compounds in toluene at room temperature resulted in no reaction. Replacing the toluene with CHCl_3 , to aid in the dissolution of Vaska's complex, did not affect the ^{11}B - or ^{119}Sn -NMR spectra. Stirring the two together for an extended period merely resulted in the slow decomposition of the starting material, as did heating the solution to reflux.

Steric effects are most likely the reason for the failure of 3.2 to react with Vaska's compound. The unusual inertness of 3.2 compared to other mono-alkyl tin trichlorides, as discussed above, is certainly an indication of a steric deactivation, towards both decomposition and further reaction. That the product 3.2 is largely kinetically and not thermodynamically stabilized is evidenced by its ready decomposition in warm solvents. Furthermore, $\text{tmpB}=\text{CR}_2$ is itself a kinetically stabilized system. That adducts thereof are inert towards further reaction is not surprising. Indeed, there are certain steric limits, readily reached by the starting amino-fluorenylidene-borane, and several have already been described (see, eg.,

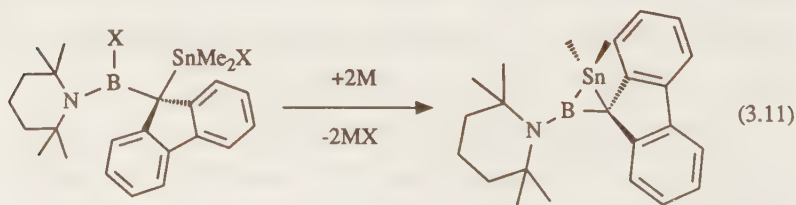
Chapter 1, reactions with $t\text{BuPCl}_2$, tmpPCl_2).

3.2.3 Reaction of $\text{tmpB}=\text{CR}_2$ with Dialkyl- and Trialkyl-Tin(IV) Halides

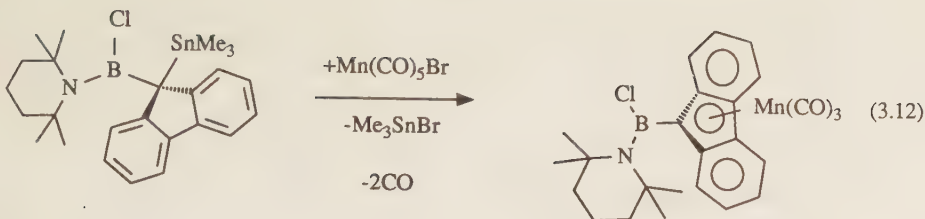
Me_2SnCl_2 adds across the $\text{B}=\text{N}$ triple bond to yield the non-cyclic product $\text{tmpB}(\text{Cl})\text{N}^t\text{Bu}(\text{SnMe}_2\text{Cl}_2)^{19}$. In addition, Me_2SnCl_2 and Me_2SnBr_2 form Lewis-acid-base adducts (according to eq.3.10); all these halides are, therefore, established Lewis acids.



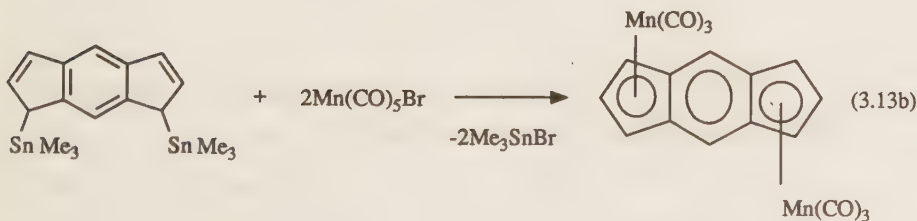
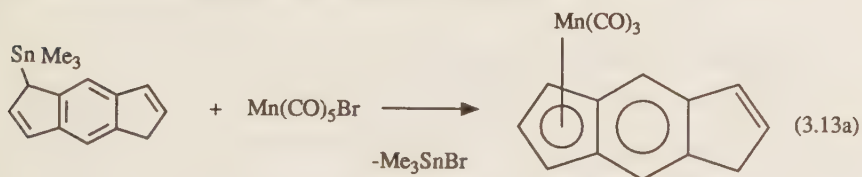
Because $\text{tmpB}=\text{CR}_2$ did react readily with SnCl_4 , it was hoped that the same would hold true for dimethyl- and trimethyl-tin(IV) halides. Furthermore, each product could prove to have its own synthetic utility: The insertion product of Me_2SnX_2 could be used an educt for the synthesis of a B-C-Sn 3-membered ring (eq. 3.11).



An even more interesting prospect would be for the use of the Me_3SnCl adduct as a building block for the [9-(amino(chloro)boryl]fluorenyl) $\text{Mn}(\text{CO})_3$ complex (according to eq. 3.12).



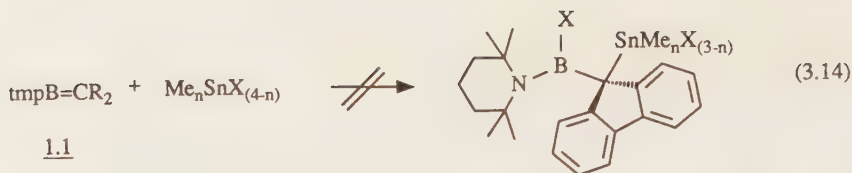
Such a transmetalation reaction *via* compounds of trimethyl tin and $\text{Mn(CO)}_5\text{Br}$ has recently been used⁴³⁾ in the synthesis of (s-indacene)(Mn(CO)_3) and (s-indacene)(Mn(CO)_3)₂ (according to eq. 3.13a and 3.13b).



These reactions were found to be very clean, high-yield syntheses of the desired complexes. Attempts to synthesize these two complexes by reacting the mono- and dianions of s-indacene with $\text{Mn(CO)}_5\text{Br}$ were unsuccessful.

Unfortunately, however, tmpB=CR_2 and Me_2SnCl_2 , Me_2SnBr_2 , and Me_3SnCl do not react according to eq. 3.14.

Even heating tmpB=CR_2 and Me_2SnBr_2 in toluene for several hours resulted in no apparent reaction (by ^{119}Sn -, ^{11}B -NMR). The reason for this poor reactivity most likely lies in the weak Lewis-acid character of dialkyl and trialkyl tin(IV) halides. By comparison, Me_3SnCl failed to react with $\text{tmpB}\equiv\text{N}^t\text{Bu}^{19)}$ in



$n = 2, \text{X} = \text{Cl}, \text{Br}$

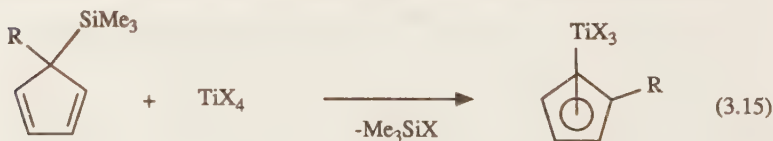
$n = 3, \text{X} = \text{Cl}$

contrast to Me_2SnCl_2 and MeSnCl_3 , clearly indicating that $\text{tmpB}=\text{C}_{13}\text{H}_8$ is too weak a base.

3.3 Reaction of $\text{tmpB}=\text{CR}_2$ with Titanium (IV) Compounds

3.3.1 Reaction with Titanium Tetrachloride and Titanium Tetrabromide

The synthesis of CpTiCl_3 and CpTiBr_3 has been found to be difficult when NaCp or LiCp is used. The reagents tend to be far too reactive and lead almost exclusively to the formation of Cp_2TiX_2 . An elegant route to the mono-cyclopentadienyl titanium trihalide species was discovered in 1980 by Clark, *et al.*³²⁾ They first synthesized (trimethylsilyl)cyclopentadiene and then carried out careful 1:1 stoichiometric reactions between this reagent and TiX_4 (eq. 3.15).



$\text{X} = \text{Cl}, \text{Br}, \text{I}$

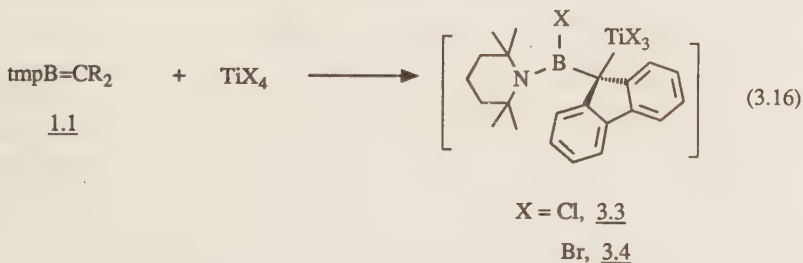
$\text{R} = \text{H}, \text{SiMe}_3$

They found that refluxing or long reaction times did not adversely affect

the yields. They furthermore were able to apply this method to the syntheses of CpTaCl_4 and CpNbCl_4 , though the products were difficult to characterize because of their low solubility.

Like $(\text{Me}_3\text{Si})\text{C}_5\text{H}_4\text{R}$, $\text{tmpB}=\text{CR}_2$ contains a labile element-carbon bond which, it has already been shown, can be cleaved by Lewis acids, resulting in the formation of an element-halogen bond (B-Cl or B-Br) and a carbon-metal bond. Just as TiX_4 ($\text{X} = \text{Cl}, \text{Br}$) ruptures the Si-C bond in Me_3SiCp to yield Me_3SiCl , it would be expected that the same reaction carried out with $\text{tmpB}=\text{CR}_2$ would rupture one B-C bond, thereby yielding the boryl-substituted (η -fluorenyl) TiX_3 : a derivative of the elusive (see section 3.1) fluorene analogue of CpTiX_3 .

Indeed, addition of TiCl_4 or TiBr_4 to a toluene solution of $\text{tmpB}=\text{CR}_2$ results in immediate exothermic reaction to the 1:1-products 3.3 and 3.4 (eq. 3.16), which precipitate from the solutions. They are adequately soluble in CHCl_3 and CH_2Cl_2 to allow for crystallization and full characterization by NMR. NMR data of the compounds 3.3 and 3.4 are given in Tables 16-18.



The ^{11}B -NMR spectra of 3.3 and 3.4 immediately indicate that the compounds are significantly different from all other metal-halide insertion products synthesized up to this point. (The unique nature of 3.3 and 3.4 was actually first apparent from their dark-green colors. All other adducts had been colorless or slightly yellow.) $\delta^{11}\text{B}$ for 3.3 is 38.8 ppm and for 3.4, 39.1 ppm. Both represent much better shielding than in the halogeno(organyl)(tmp) boranes so far discussed. The reason for this could be greater π - π overlap between boron and the tmp nitrogen atom. If this is the case, a significant amount of B=N double bond character would be expected, and this should be further demonstrated by the ^1H - and ^{13}C -NMR spectra.

In fact, the ^1H -NMR spectra of 3.3 and 3.4 indicate the presence of two sets of magnetically non-equivalent methyl-groups (singlets are found at $\delta^1\text{H} = 0.95$ ppm and 0.93 ppm for 3.3 and 3.4, respectively, but these singlets integrate to only 6 protons). This is a phenomenon often found in compounds in which rotation about the B-N bond is hindered because of increased double bond character¹⁹).

Further evidence in support of asymmetry imposed by increased B=N character is found in the ^{13}C -NMR spectrum of 3.3. (3.4, though soluble in CDCl_3 and CD_2Cl_2 , was not soluble enough to obtain a ^{13}C -NMR spectrum.) In the aliphatic region, seven different signals are found, assignable to individual C-atoms in the tmp moiety. Such asymmetry is found when rotation about B-N is significantly hindered.

Otherwise, the ^1H -NMR spectrum of 3.3 and 3.4 reveal little information about the nature of the bonding between the fluorenyl ligand and TiX_3 except to indicate the lack of proton involvement: The proton resonances of $\delta^1\text{H} = 7.29$ -8.28 ppm are slightly downfield but not significantly different from the fluorene proton resonances found in other metal-halide addition products.

The ^{13}C -NMR spectrum of 3.3, however, offers significant structural clarification. The aliphatic region's lack of symmetry was just discussed. In the aromatic region, the symmetry of the starting material $\text{tmpB}=\text{CR}_2$ is preserved: namely, six signals are found for the C-atoms of both rings. However, the signal positions differ drastically from those in other insertion compounds: no signal is found further upfield than $\delta^{13}\text{C} = 125.6$ ppm and none is further downfield than $\delta^{13}\text{C} = 131.6$ ppm. Such an arrangement implies significant deshielding of the H-bound C-atoms and a strong shielding of the quaternary C-atoms. This phenomenon can be explained by a greater delocalization of electron density across all three rings, decreasing electron density in the outer rings and increasing it in the central five-membered ring. The result is an average, delocalized effect, and all C-atoms in the ^{13}C -NMR spectrum are found within a very small region (^{13}C -NMR range = 6.0 ppm).

This tremendous upfield shift for C10 and C15 ($\delta^{13}\text{C} = 131.3, 131.6$ ppm, respectively, compared to $\delta^{13}\text{C} = 140.2$ and 141.3 ppm for the GeCl_4 adduct, 3.1)

can most reasonably be explained by a strong Ti-C interaction for these two C-atoms, implying a η^5 -type coordination (Fig. 3.2):

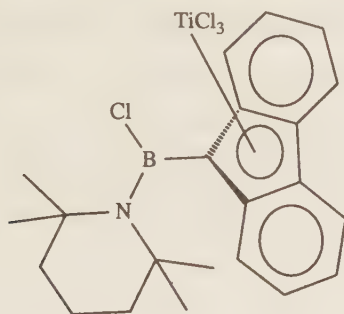


Fig. 3.2

This would, of course, be fully analogous to $(\eta^5\text{-Cp})\text{TiX}_3$, whose formation from Me_3SiCp and TiX_4 has already been discussed as being similar to the formation of 3.3 and 3.4.

As was discussed in section 3.1, neither $(\eta^5\text{-fluorene})\text{TiCl}_3$ nor $(\eta^5\text{-fluorene})_2\text{TiCl}_2$ has ever been fully characterized, and, therefore, neither ^1H - nor ^{13}C -NMR spectra are available for comparison. Although $(\eta\text{-fluorenyl})_2\text{ZrCl}_2$ has been characterized by X-ray methods, no ^{13}C - or ^1H -NMR spectrum was described. However, Basolo, *et al.* did report a ^{13}C -NMR spectrum of $(\eta^5\text{-fluorenyl})\text{Mn}(\text{CO})_3$ as well as that of a $(\eta^1\text{-fluorenyl})\text{Mn}(\text{CO})_3(\text{PR}_3)_2$ derivative. They found that, upon coordination of Mn to the quaternary C-atoms of the fluorenyl ligand, an upfield ^{13}C -NMR shift of *ca.* 40 ppm is observed (from 140 to 100 ppm). Although the upfield shift in 3.3 is not as large, it should be noted that the C-atoms of the Cp ligand, when coordinated to Ti(IV), are found much further downfield than in $\text{CpMn}(\text{CO})_3$ ^{33,34}. Furthermore, as in 3.3, the H-bound C-atoms of the fluorenyl ligand are deshielded to the extent that the high-field resonance at $\delta^{13}\text{C} = 120$ ppm is no longer found in the compound $(\eta^5\text{-fluorenyl})\text{Mn}(\text{CO})_3$. It is shifted *ca.* 5 ppm downfield. This agrees well with the result found for 3.3, for which the signal furthest upfield lies at $\delta^{13}\text{C} = 125.6$ ppm.

The ^{11}B -, ^1H - and ^{13}C -NMR data for 3.3 and 3.4 are summarized in tables

16, 17 and 18, with data for (η^5 -fluorenyl) $Mn(CO)_3$ ³⁵.

Although 3.4 could only be characterized by analysis, mass spectroscopy, ¹¹B- and ¹H-NMR, its similar color to 3.3 (both are dark green), its similar behavior in solution (both are soluble only in CH₂Cl₂ as the 1:1 adduct), and its similar ¹¹B- and ¹H-NMR spectra led to believe that it also contains a η^5 -coordinated fluorenyl ligand. Furthermore, TiBr₄ and TiCl₄ both reacted exothermically with (SiMe₃)Cp to yield CpTiX₃ (X=Cl, Br), both of which contain η^5 -coordinated Cp ligands³².

Table 16: ¹¹B-NMR Data of the Products 3.3 and 3.4 (in ppm; half-widths in Hz; solvents numbered as in Table 1)

<u>Add. of</u>	<u>Nr.</u>	<u>$\delta^{11}B$</u>	<u>$h_{1/2}$</u>	<u>Solvent</u>
TiCl ₄	<u>3.3</u>	38.8	500	1
TiBr ₄	<u>3.4</u>	39.1	510	1

Table 17: ¹H-NMR Data of the Products 3.3 and 3.4 (in ppm; solvents as in Table 16)

<u>Add. of</u>	<u>Nr.</u>	<u>CH₃</u> (tmp)	<u>CH₂</u> (tmp)	<u>arom. H</u> (fluorene)
TiCl ₄ ^a	<u>3.3</u>	0.95-1.88		7.29-7.74
TiBr ₄ ^a	<u>3.4</u>	0.93-1.76		7.29-8.28

a. CH₂Cl₂ signal also found, but omitted here for clarity.

Table 18: ^{13}C -NMR Data of the Aromatic Region in 3.3, the η_1 -Coordinated Product 1.2, and $(\eta_5\text{-fluorenyl})\text{Mn}(\text{CO})_3$ (in ppm; numbering scheme as in Fig. 1.1; in CDCl_3)

<u>Compound</u>	<u>C10</u>	<u>C15</u>	<u>C11</u>	<u>C12</u>	<u>C13</u>	<u>C14</u>
$(\eta_5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3^{\text{a}}$	95.2	106.1	124.9	127.7	127.7	124.5
<u>3.3</u>	131.6	131.3	129.8	130.2	130.9	125.6
<u>1.2</u> ^b	142.8	141.6	125.3	127.0	127.4	120.1

a. Lit.: 35.

b. See Chapter 1, Table 3.

3.3.1.1 X-ray Crystal Structure of $\text{tmpBCl}(\eta\text{-fluorenyl})\text{TiCl}_3$, 3.3

Crystals of 3.3 can be obtained from CH_2Cl_2 solutions at -20°C in the form of dark green needles of the 1:1 CH_2Cl_2 adduct (by ^1H -NMR and C,H,N analysis) suitable for X-ray crystallography. 3.3 crystallizes in the monoclinic system, with space group $\text{P2}_{1/n}$, $Z = 4$.

An ORTEP plot of 3.3 is depicted in Fig. 3.3. Selected bond lengths and angles are listed in Tables 19 and 20, respectively.

The B-N bond length of $1.367(23) \text{ \AA}$ corresponds to a B-N double bond and, thus, explains the hindered rotation about the B-N bond implicit in the ^1H - and ^{13}C -NMR spectra. In addition, the $\text{tmp-C}_2\text{-N}$ -plane is found to be nearly coplanar with the N-B-Cl-C1-plane, which itself is nearly perpendicular to the plane of the fluorenyl five-membered ring. This is further evidence for a B=N double bond, allowing for efficient electronic saturation of the boron atom through $\pi\text{-}\pi$ overlap. (For comparison, B-N in tmpB=CR_2 was found to be $1.353(3) \text{ \AA}$. In this case, because of the hetero-allene structure and the near linearity of the N-B-C unit, a large amount of B=N double-bond character can be assumed³⁶.)

The B-Cl distance of $1.841(17) \text{ \AA}$ is very similar to that found in 1.2,

tmpBCl(C₁₃H₉PCl₂)(B-Cl = 1.820(3) Å, see 1.2.1.2).

The B-C(1) bond length of 1.601(21) Å represents a lengthening of 18 pm compared to the starting fluorenylidene-borane (B-C(1) = 1.42.4(3) Å) and lies in the region expected for B-C single bonds. (Compare B-C(1) in tmpBF(C₁₃H₁₀): 1.589(3) Å)³⁶.)

Looking at the Ti-C distances, the first noticeable feature is the rather broad range over which they fall. The Ti-C(1) distance is the shortest at 2.296(17) Å, the longest Ti-C bond is to C(8): 2.528(16) Å. The three C-atoms closest to the boron atom are more tightly bound to Ti than are the two C-atoms at the back of the ring. This might imply a certain amount of η^3 -(π -allylic)-character in the bonding of the fluorenyl ligand to Ti. However, the difference between the longest and the shortest Ti-C bond of 23 pm is still much smaller than that found in the "true" η^3 -fluorenyl complex: (η^5 -fluorenyl)(η^3 -fluorenyl)ZrCl₂, for which the bond lengths were found to lie 42 pm apart. Furthermore, the spread of 23 pm found in 3.3 for Ti-C bond lengths is actually **smaller** than the spread found for the η^5 -fluorenyl ligand in the same Zr-complex: 25 pm¹⁰). This relatively asymmetric binding of Ti to the five carbon atoms can be attributed to the inherent tendency of electron density in the fluorenyl ligand to localize at C(1), resulting in an asymmetrical distribution throughout the five-membered ring. The bonding of TiCl₃ to (C₁₃H₉)B(Cl)tmp can be viewed as an asymmetric η^5 -coordination. That the coordination is η^5 - and not η^3 - was already inferred from the ¹³C-NMR spectrum in which all C-atoms of the central five-membered ring were found to be shifted upfield.

Table 19: Selected Bond Lengths (in Å) in 3.3. The atoms are numbered as in the ORTEP Plot (Fig. 3.3)

Ti	-Cl(1)	2.256(5)	Ti	-Cl(2)	2.214(5)
Ti	-Cl(3)	2.226(5)	Ti	-C(1)	2.296(17)
Ti	-C(2)	2.361(16)	Ti	-C(13)	2.436(18)
Ti	-C(7)	2.491(17)	Ti	-C(8)	2.528(16)
B	-C(1)	1.601(21)	B	-N	1.367(23)
B	-Cl(4)	1.841(17)			

Table 20: Selected Bond Angles (in degrees) in 3.3. The atoms are numbered as in the ORTEP Plot (Fig. 3.3)

Cl(1)	-Ti	-Cl(2)	101.8(2)	Cl(1)	-Ti	-Cl(3)	98.8(2)
Cl(2)	-Ti	-Cl(3)	104.7(2)	Cl(4)	-B	-C(1)	109.5(12)
Cl(4)	-B	-N	122.5(11)	C(1)	-B	-N	128.1(13)

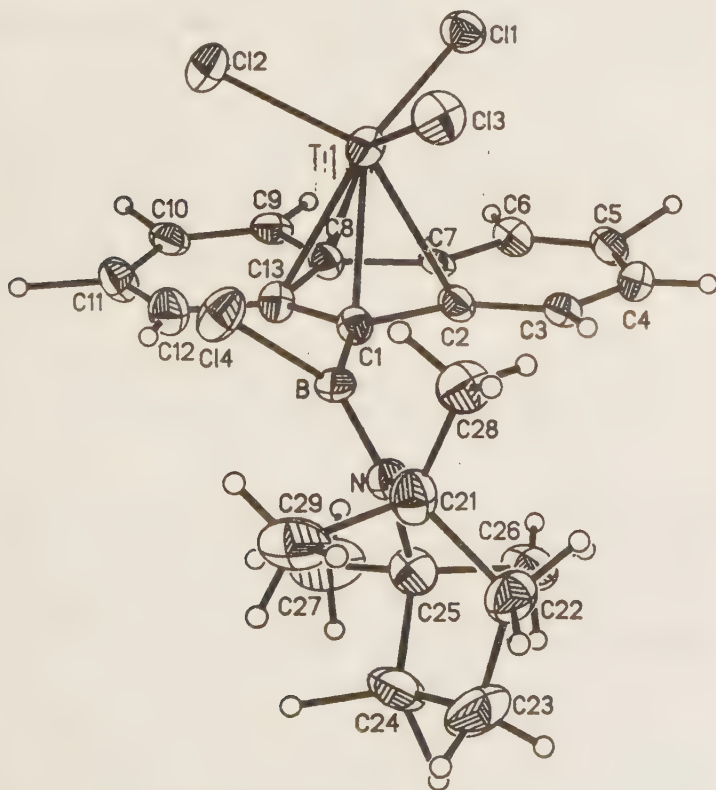
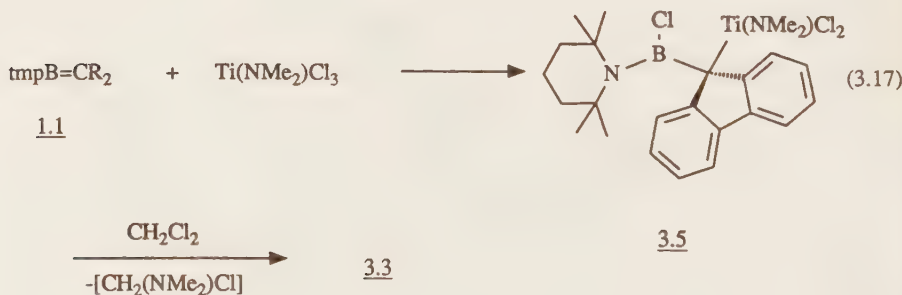


Fig. 3.3: ORTEP Plot of the compound 3.3

3.3.2 Reaction with (Dimethylamino)titanium Trichloride

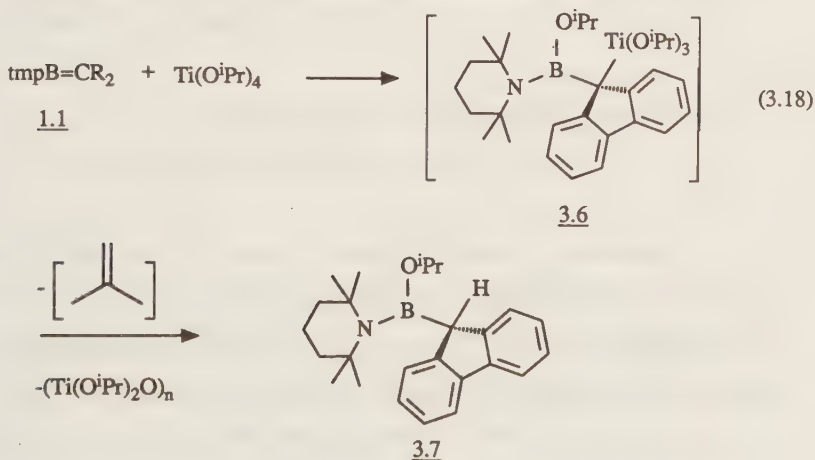
As with $\text{P}(\text{NMe}_2)\text{Cl}_2$, it was hoped that reaction of $(\text{Me}_2\text{N})\text{TiCl}_3$ with $\text{tmpB}=\text{CR}_2$ would lead to an addition product whose constitution would provide evidence for the relative tendencies of the NMe_2 - versus the Cl -substituent bound to titanium to be transferred to boron. In addition, it was hoped that the presence of a NMe_2 moiety would enhance the solubility of the addition product relative to 3.3 and 3.4. Reaction of $\text{tmpB}=\text{CR}_2$ with $(\text{Me}_2\text{N})\text{TiCl}_3$ produces a largely insoluble, light green product, presumably 3.5 (eq. 3.17). However, the product dissolved only in CH_2Cl_2 to yield a dark green solution from which, upon cooling to -20°C , the TiCl_4 product, 3.3, separated. Presumably 3.5 reacts with CH_2Cl_2 in a halogen-amino exchange reaction; this would explain its excellent "solubility" in CH_2Cl_2 . No side products could be isolated.



That Cl and not NMe_2 migrates in the initial reaction was assumed because of a) the known high tendency for Cl to be transferred from Ti to B as evidenced by the exothermic formation of 3.3 and b) the formation of the chloro-addition product in the analogous reaction with $\text{tmpB}\equiv\text{N}^t\text{Bu}^{37)}$.

3.3.3 Reaction with Isopropyl Titanate

In a further attempt to study the substituent influence of TiX_4 -compounds, reaction was carried out between $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{tmpB}=\text{CR}_2$. The expected product, 3.6, was not obtained, though reaction did occur to a single boron-containing product (^{11}B -NMR) after only 6 hours (eq. 3.18). The product 3.6 may very well have been formed, or at least a Lewis acid-base adduct, from which isopropene could be eliminated with simultaneous proton transfer to C9 of the fluorenyl ligand. The resulting product, 3.7 (in effect, the isopropanol addition product of $\text{tmpB}=\text{CR}_2$) could be fully characterized by analysis and NMR.



Attempts to isolate $(\text{Ti}(\text{O}^i\text{Pr})_2\text{O})_n$ by distillation only resulted in traces of $\text{Ti}(\text{O}^i\text{Pr})_4$.

The ^{11}B -NMR spectrum of 3.7 corresponds to an alkoxy(organyl)(tmp) borane. The MeOH adduct of $\text{tmpB}=\text{CR}_2$ has a ^{11}B -NMR signal at $\delta^{11}\text{B} = 34.3$ ppm ($h_{1/2} = 400$ Hz)³⁶, that of 3.7 lies at 31.5 ppm ($h_{1/2} = 330$ Hz). The ^{13}C - and ^1H -NMR spectra do not show any unusual structural features. The C9-bound H-atom is found at $\delta^1\text{H} = 4.34$ ppm, and this agrees well with that found in the MeOH adduct ($\delta^1\text{H} = 4.44$ ppm). The quaternary C-atoms of the tmp ring in 3.7 produce a ^{13}C -NMR signal at $\delta^{13}\text{C} = 53.2$ ppm, which lies at higher field as compared with the adducts of the metal halides (in general: $\delta^{13}\text{C} \cong 57\text{--}58$ ppm). In

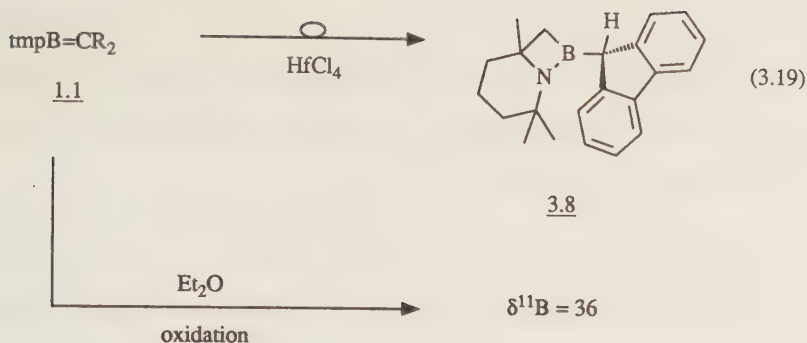
the MeOH adduct, a similar high field shift ($\delta^{13}\text{C} = 53.3$ ppm) is observed³⁶). This is explained by the presence of an O-atom instead of a much more electronegative halogen atom. This results in less electron density being removed from the boron atom, and, therefore, less electron density (less B-N $\pi\pi$ - $\pi\pi$ overlap) is required from the nitrogen of the tmp ring for electronic saturation of the boron atom. The presence of strongly electron withdrawing substituents on tmp boranes tends to decrease the shielding of C2,6 of tmp. The $\Delta\delta^{13}\text{C}$ value for C2,6 of *ca.* 5 ppm between 3.7 and 3.3 (for which a large amount of B=N double bond character could be demonstrated) provides an excellent example of this phenomenon.

3.4 Reaction of tmpB=CR₂ with Hafnium Tetrachloride

Recognizing the electronic similarities between TiX_4 and HfX_4 , it was hoped that the addition product of HfCl_4 could be obtained in analogy to TiCl_4 . Because HfCl_4 is much less Lewis-acidic and possesses a non-molecular structure in the solid state, reaction was carried out in Et_2O , a polar coordinating solvent.

However, we observed no reaction between HfCl_4 and tmpB=CR₂ in ether at room temperature. Heating to reflux for several days yields two products according to ^{11}B -NMR ($\delta^{11}\text{B} = 42, 36$ ppm). HfCl_4 can be retrieved nearly quantitatively. No product can be isolated from the reaction mixture. The most likely paths are those shown in eq. 3.19.

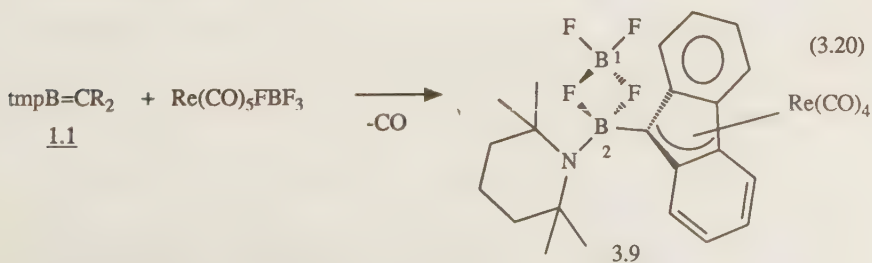
$\delta^{11}\text{B}$ of 3.8 is found at 42 ppm and is most likely a rearrangement product, formed catalytically by transition metal halides. The rearrangement was first observed using RhCl_3 as the metal halide³⁸). In addition we have shown that this can also be effected by NiCp_2 , CoCp_2 ³⁹) and by transition metal olefin complexes (see section 5.6 of this work). The other side reaction, oxidation of tmpB=CR₂ in refluxing solvents, has been shown to occur in toluene, hexane, pentane, CHCl_3 , CH_2Cl_2 , Et_2O and THF. The exact nature of the product has been studied, but the



structure is not known with certainty⁴⁰.

3.5 Reaction with Pentacarbonylrhenium Tetrafluoroborate

Since tmpB=CR_2 is a weak Lewis base its reaction with a strong organometallic Lewis acid such as $\text{Re(CO)}_5\text{FBF}_3$ ⁴¹) was investigated. In cooperation with P. Fritz and E. Fritsch, the reaction between $\text{Re(CO)}_5\text{FBF}_3$ and tmpB=CR_2 was studied at room temperature. A light yellow powder, soluble in nearly all organic solvents was obtained. Allowing an ether/pentane solution to evaporate slowly led to the formation of crystals which were placed on a diffractometer and data were collected. The structure could not be solved. However, based on spectroscopic data and analysis, the product could be depicted as 3.9 (eq.3.20).



The ¹¹B-NMR spectrum of 3.9 indicates the presence of two B-atoms, one

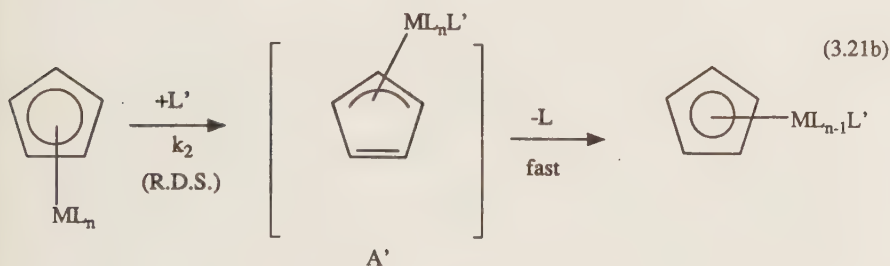
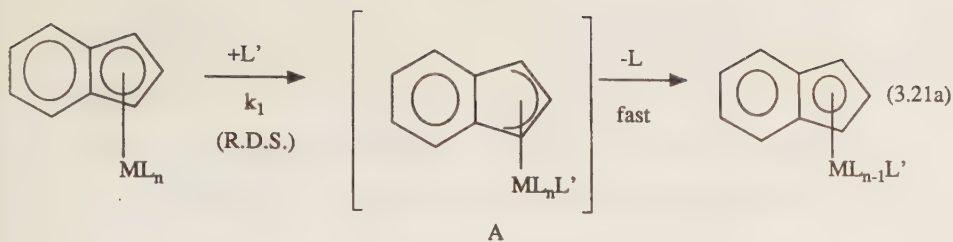
at $\delta^{11}\text{B} = 1.1$ ppm ($h_{1/2} = 124$ Hz) and one at -1.0 ppm ($h_{1/2} = 33$ Hz) of relative intensity $I = 1:1$. Thus, both B-atoms are four-coordinate, with one signal being sharper and slightly further downfield than the other. This would correspond well with a BF_4 -unit attached to another boron atom, the latter of which has less electronegative substituents (B1 and B2 in 3.9).

The ^{13}C -NMR spectrum indicates the presence of a tmp unit in a symmetrical environment with free rotation about the B-N axis. The aromatic region, however, indicates a complete lack of symmetry: 12 different ^{13}C -NMR signals are found. However, as would be expected for metal coordination to the central ring, the ^{13}C -NMR signals at 140 and 145 ppm have disappeared, and all aromatic ^{13}C -NMR signals are spread over a range of only 15 ppm. The signal at $\delta^{13}\text{C} = 135.0$ ppm can be assigned to a non-Re-bound quaternary C-atom, as can the signal at $\delta^{13}\text{C} = 129.3$ ppm. All other signals lie in the normal aromatic region, and the asymmetrical allylic bonding mode agrees well with the loss of symmetry in this region.

The ^{13}C -NMR resonance for the Re-bound CO-ligands is observed at $\delta^{13}\text{C} = 192.4$ ppm. The I.R. spectrum indicates a tetracarbonyl compound. Furthermore, though $\nu(\text{B-F})$ absorptions are found in the I.R. spectrum of 3.9, the symmetrical BF_4 absorptions found in ionic species (such as the starting material) are not present.

Although the η^3 -fluorenyl complex known in the literature¹⁰⁾ contains a fluorenyl-ligand which is symmetrically bound to the metal (ie. C9, C10, C10'), the non-symmetrical coordination in the proposed structure can be corroborated by the subsequent complete aromatization and, hence, stabilization of one of the six-membered rings⁴²⁾. This argument has been used by Basolo to explain rate enhancement in associative ligand replacement reactions in indenyl *versus* cyclopentadienyl systems (eq. 3.21a and 3.21b)¹⁶⁾.

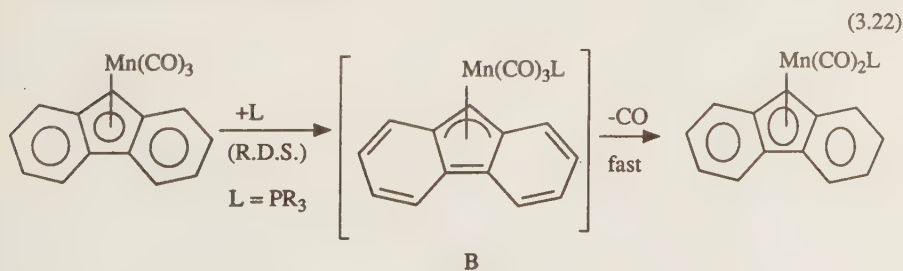
The rate enhancement, also known as the "indenyl ligand factor"¹⁷⁾, has been explained by assuming an aromatic stabilization of the η^3 -indenyl transition



$$k_1 \sim 10^8 k_2$$

state A, not possible in the unsubstituted cyclopentadienyl system.

Although η^3 -fluorenyl species have been proposed as intermediates in ligand substitution reactions of $(\eta^5\text{-fluorenyl})\text{Mn}(\text{CO})_3$ ¹⁷(eq. 3.22, B) their existence has never been proven.



(as drawn by Basolo, *et al.*
in ref. 17)

However, based on evidence in the literature, our proposed asymmetrical $(\eta^3\text{-fluorenyl})\text{Re}(\text{CO})_4$ complex, 3.9, should also be a reasonable consideration for the structure of this elusive intermediate B. Basolo, *et al.* assume the symmetry of

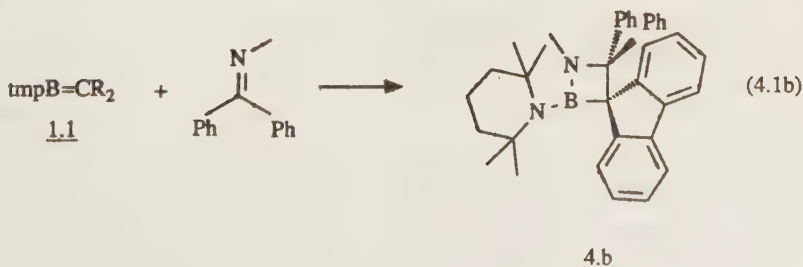
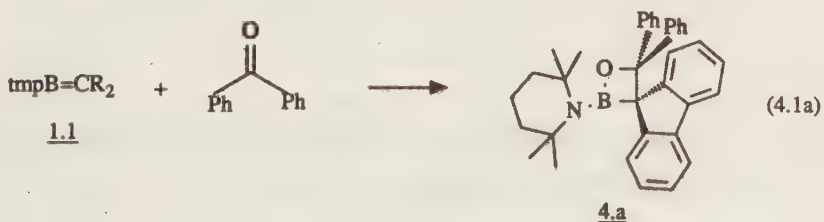
the η^3 -intermediate but fail to discuss how this ties in with the aromaticity argument invoked for the indenyl system. This is in spite of the fact that the $(\eta^5\text{-fluorenyl})\text{Mn}(\text{CO})_3$ system reacts 1000 times **faster** than the indenyl system¹⁷). A structural determination of 3.9 could provide an answer, or at least some direction, to this very interesting chemical question⁴⁴).

Chapter 4:

(2+2) Cycloaddition Reactions

4.1. Introduction

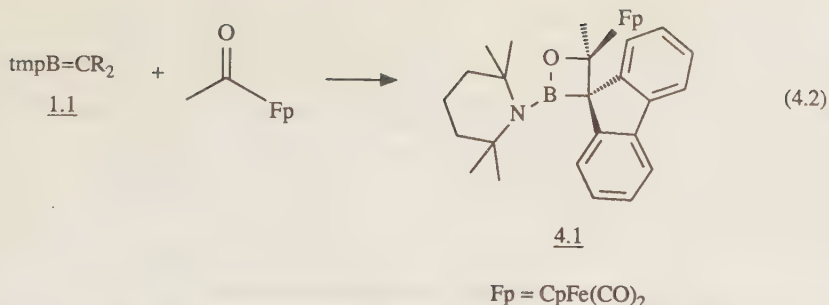
One of the important reactions of ketenes are (2+2) cycloadditions to yield four-membered ring systems¹⁾. Having demonstrated analogies between ketenes and the alkylidene borane $\text{tmpB}=\text{CR}_2$, Glaser carried out a series of cycloadditions with $\text{tmpB}=\text{CR}_2$ to yield four-membered boron-containing heterocycles²⁾. As examples, diphenylketene (eq. 4.1a), benzophenone-N-methylimine (eq. 4.1b), and 1-diethylamino-1-propyne (eq. 4.1c) were shown to undergo rapid addition reactions to yield oxaboretanes, azaboretidines and boretenes, respectively.



The purpose of the present work was to expand upon the efforts of previous workers to include cycloadditions at ligands attached to transition metals, and to include carbonyl compounds carrying additional functional groups such as amino acids, acid chlorides, esters and, finally, transition metal carbene complexes.

4.2.1 Reaction with $\text{CpFe}(\text{CO})_2\text{COCH}_3$

Addition of $\text{CpFe}(\text{CO})_2\text{COCH}_3$ to a toluene of $\text{tmpB}=\text{CR}_2$ leads rapidly to the cycloadduct, 4.1 (eq. 4.2), which can be isolated as a stable, orange-yellow crystalline solid from toluene:hexane at -20°C . It was characterized by analysis, NMR, I.R. and mass spectroscopy. NMR data for 4.1 are listed in Tables 21-23.



The mass spectrum contains the parent peak at $m/e = 535$ (^{11}B , ^{56}Fe), albeit with low intensity (ca. 1 %). Two fragments at $m/e = 507$ and 479 correspond to the loss of one and two CO ligands, respectively. These peaks are found with relatively high intensity (5% and 25%, respectively), and their isotope patterns agree well with calculated patterns. The most intense peak is found at $m/e = 358$, corresponding to the $(\text{M}-(\text{CpFe(CO)}_2))^+$ fragment. The stability of this fragment will prove to be of interest in discussions of the reactivity of 4.1 (see next section).

The ^{11}B -NMR signal at $\delta^{11}\text{B} = 37.2$ ppm ($h_{1/2} = 460$ Hz) is not significantly different from that found for other oxaboretanes synthesized from tmpB=CR_2 and ketones. The benzophenone cycloadduct is found at $\delta^{11}\text{B} = 36.9$ ppm²⁾, acetone yields an oxaboretane with $\delta^{11}\text{B} = 35.8$ ppm³⁾.

Further support for the suggested structure of 4.1 comes from the ^1H -NMR and ^{13}C -NMR spectra. The protons of the tmp ring are found in seven well-divided groups between $\delta^1\text{H} = 0.40$ and 1.82 ppm. Such a division of signals indicates both hindered rotation about the B-N bond, resulting in the inequivalence of C3 and C5 protons, as well as of the methyl protons of C7 and C7' (or C8 and C8'). Since there are two signals for C7 and C8 one can conclude that there is no plane of symmetry perpendicular to the fluorene ring.

This result is further substantiated by the ^{13}C -NMR spectrum in which eight different signals are found for the nine tmp C-atoms. 2 of the 4 signals corresponding to the tmp methyl groups apparently fall together. This is apparent from the larger intensity (ca. twice) found for the signal at $\delta^{13}\text{C} = 33.1$ ppm compared to the other signals.

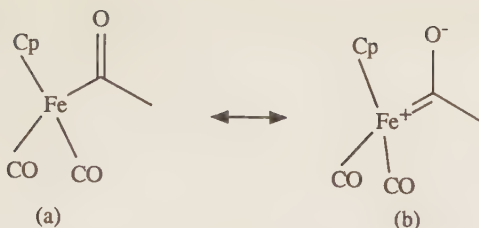
The ^1H -NMR spectrum contains two additional signals at $\delta^1\text{H} = 2.48$ ppm (3H) and $\delta^1\text{H} = 3.53$ ppm (5H) for the acyl methyl group and the Cp protons, respectively. The signal for the CH_3CO group in the starting material does not differ significantly from that found in the cycloadduct ($\delta^1\text{H}(\text{CH}_3) = 2.38$ ppm). The Cp protons are, however, shielded by 0.67 ppm relative to $\text{CpFe}(\text{CO})_2\text{COCH}_3$ ($\delta^1\text{H}(\text{Cp}) = 4.20$ ppm)⁴). The corresponding signals in the ^{13}C -NMR spectrum are also found, and they do not differ drastically from those found for $\text{CpFe}(\text{CO})_2\text{COCH}_3$ ($\delta^{13}\text{C}(\text{CH}_3) = 47.9$ ppm; S.M. = 52.0 ppm; $\delta^{13}\text{C}(\text{Cp}) = 84.8$ ppm; S.M. = 86.9 ppm)⁵). The only major difference is found for the ketonic C-atom, which is shifted from $\delta^{13}\text{C} = 254.4$ ppm to $\delta^{13}\text{C} = 103.4$ ppm in the oxaboretane 4.1. This latter signal is still far downfield from the methyl group found in $\text{MeFeCp}(\text{CO})_2$ ($\delta^{13}\text{C} = -23.5$ ppm)⁵). The drastic shift from 254.4 to 103.4 ppm results from the change in hybridisation.

The fluorenyl region of the ^{13}C -NMR spectrum indicates the lack of a plane of symmetry perpendicular to the fluorenyl ring system. 11 different signals are found for the 12 C-atoms of the two six-membered rings. Two of the aromatic signals between $\delta^{13}\text{C} = 126.0$ and 128.6 ppm coincide. C10 and C10' lie the farthest apart from each other with $\Delta\delta^{13}\text{C} = 7.0$ ppm. C15 and C15', being further away from the center of assymetry at C9, lie only 1.6 ppm apart. As would be expected, C14 and C14' are even closer together, being separated by only 0.6 ppm.

The signals for the CO-ligands form a broad peak at $\delta^{13}\text{C} = 208.0$ ppm, representing a high field shift of 7.7 ppm as compared with the starting material⁵).

The I.R. spectrum indicates the presence of two CO groups with absorption bands at $\nu(\text{C}\equiv\text{O}) = 2000\text{ cm}^{-1}$ and $\nu(\text{C}=\text{O}) = 1945\text{ cm}^{-1}$ (Fig. 4.1). Otherwise, the region between 1500 cm^{-1} and 2600 cm^{-1} is free of any bands. Thus, the $\nu(\text{N}=\text{B}=\text{C})^2$ at 1717 cm^{-1} and the acyl $\nu(\text{C}=\text{O})^4$ at 1655 cm^{-1} have both disappeared as would be expected for the product 4.1. Further more, the $\text{C}\equiv\text{O}$ absorptions are at lower frequency than in the starting material, being found in the region expected for other (alkyl)Fe(CO)₂Cp complexes⁶). This is easily explained by the resonance structures (a) and (b) for $\text{CpFe}(\text{CO})_2\text{COCH}_3$:

In structure (b), electron density is removed from the metal and the $\text{C}\equiv\text{O}$



Resonance structures of FpCOCH_3 used to explain decreased electron density at the Fe center.

bond becomes stronger since $\text{Fe} \rightarrow \text{C} \equiv \text{O}$ backbonding decreases. In the product 4.1, the acyl carbon atom of the starting compound becomes sp^3 -hybridized. This eliminates resonance structure (b) ($\text{Fe}(\text{d}\pi)\text{-C}(\text{p}\pi)$ interaction no longer possible) and the $\text{C} \equiv \text{O}$ frequencies move to lower wavenumbers, as electron density at Fe is reserved for backbonding to the carbonyl ligands.

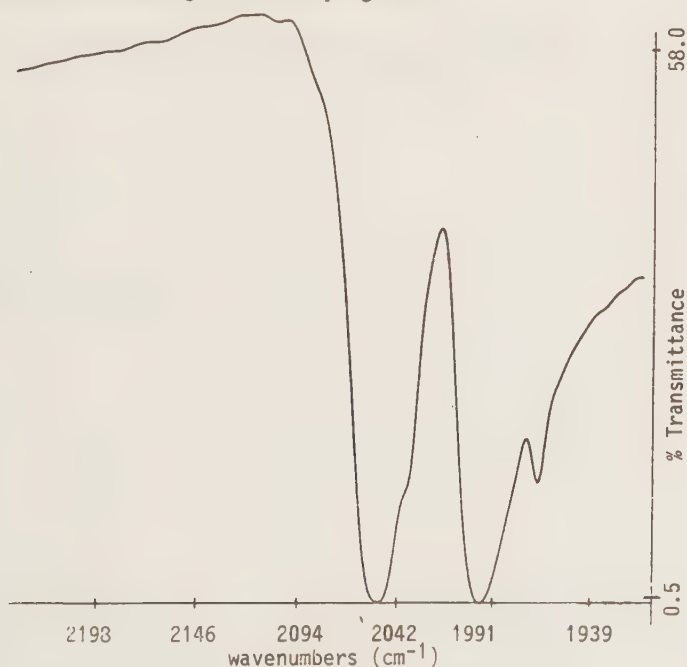


Fig 4.1: CO Region of the I.R. Spectrum of 4.1

4.2.1.1 Spectroscopic Data

The NMR data for 4.1 are listed in Tables 21-23.

Table 21: ^{11}B -NMR Data of the Cycloaddition Products 4.1 and 4.3-4.7 (in ppm; half-widths in Hz; solvents numbered as in Table 1)

<u>Add. of</u>	<u>Nr.</u>	<u>$\delta^{11}\text{B}$</u>	<u>$\hbar_{1/2}$</u>	<u>Solvent</u>
$\text{CpFe}(\text{CO})_2\text{COCH}_3$	<u>4.1</u>	37.2	460	2
CS_2^{a}	<u>4.3</u>	44.9	660	1
$\text{CpRu}(\text{PPh}_3)_2\text{C}\equiv\text{CPh}$	<u>4.4</u>	33.3	700	b
$(\text{OEt})\text{COCH}_3$	<u>4.5</u>	36.1	480	1
$(\text{NMe}_2)\text{CH}_2\text{CO}_2\text{H}$	<u>4.6</u>	6.1	135	1
ClCOPh	<u>4.7</u>	27.3	330	1

a. From the reaction between $\text{tmpB}=\text{CR}_2$ and $(\text{CpFe}(\text{CO})_2)_2\text{CS}_2$ (see text).

b. CH_2Cl_2

Table 22: ^1H -NMR Data of the Products 4.1, 4.3, and 4.5-4.6 (in ppm; solvents as in Table 21)

<u>Nr.</u>	<u>CH₃</u> (tmp)	<u>CH₂</u> (tmp)	<u>arom. H</u> (fluorene)	<u>other</u>
<u>4.1</u>	0.40-1.82		7.16-7.24(4H) 7.32-8.43(4H)	2.48 (CH ₃ -CO) 3.53 (Cp)
<u>4.3</u>	0.72(6H) 0.96(6H)	1.06-1.46	6.23-6.91 7.15-7.35 7.90-8.02	
<u>4.5</u>	1.00	1.25-1.68	7.14-7.30(4H) 7.42-7.85(4H)	1.16(6H) (CH ₃ , CH' ₃) 3.10, 3.52 (2H, CH ₂) ^a
<u>4.6</u>	1.46	1.30-1.70	7.10-7.80	2.35, 2.57 (N(CH ₃) ₂) 3.89 (2H, H-α) 4.20 (C9-H)

a. Two overlapping quintets: $J_{\text{gem}}(^1\text{H}-^1\text{H}) = 30 \text{ Hz}$

Table 23: ^{13}C -NMR Data of the Products 4.1, 4.3, and 4.5-4.7 (in ppm; solvents as in Table 21)

Table 23a: ^{13}C -Resonances of the tmp ring

<u>Nr.</u>	<u>C4</u>	<u>C7/8</u>	<u>C3/5</u>	<u>C2/6</u>	<u>other</u>
<u>4.1</u>	16.8	31.1 31.9 33.1	40.0 40.7	53.3 54.7	a
<u>4.3</u>	15.3	31.0 32.3	38.2	56.1	b
<u>4.5</u>	15.1 16.3*	31.9	39.4	57.7	c
<u>4.6</u>	15.4	28.0 36.7	34.5	44.6	d
<u>4.7</u>	14.8	32.0	36.0	54.5	e

a. 47.9 ($\underline{\text{CH}_3\text{-CO}}$), 84.8 ($\text{Fe-}\underline{\text{C-O}}$), 208.0 ($\underline{\text{CO}}$)

b. 194.8 ($\text{S-}\underline{\text{C=S}}$)

c. 22.1 ($\underline{\text{CH}_3\text{-CO}_2^-}$), 31.4 ($\underline{\text{CH}_2\text{-CH}_3}$), 53.7 ($-\underline{\text{CO}_2}$)

d. 55.1, 61.9 ($\text{N}(\underline{\text{CH}_3})(\underline{\text{C}}'\text{H}_3)$), 62.8 ($\underline{\text{C-}\alpha}$), 169.0 ($-\underline{\text{CO}_2}$)

e. 127.3, 128.6, 130.1 (phenyl), 152.0 ($\underline{\text{COC!}}$)

Table 23b: ^{13}C -Resonances of the fluorene ring

<u>Nr.</u>	<u>C9</u>	<u>C10</u>	<u>C15</u>	<u>C11</u>	<u>C12</u>	<u>C13</u>	<u>C14</u>
<u>4.1</u>	n.o.	147.7 154.7	140.4 142.0	126.0 126.4	126.8	128.4 128.6	119.4 120.0
<u>4.3</u>	n.o.	145.6 147.8	140.0 142.0	124.6 124.8	125.0 125.2	126.3	118.7 119.2
<u>4.5</u>	n.o.	145.1	140.7	125.8	126.0	128.3	119.0 119.7
<u>4.6</u>	45.6	143.1	141.6	123.6	124.9	124.9	119.7
<u>4.7^f</u>	n.o.	139.5 139.1	137.6 137.4	123.3	125.0 126.2	126.7 127.0	119.4

* contains the signal for both C4 and $\text{CH}_3\text{-CH}_2$

n.o. = not observed: boron-bound C-atom

a. 47.9 ($\text{CH}_3\text{-CO}$), 84.8 (Fe-C-O), 208.0 (CO)

b. 194.8 (S-C=S)

c. 22.1 ($\text{CH}_3\text{-CO}_2^-$), 31.4 ($\text{CH}_2\text{-CH}_3$), 53.7 ($-\text{CO}_2$)

d. 55.1, 61.9 ($\text{N(CH}_3)(\text{C}'\text{H}_3)$), 62.8 ($\text{C-}\alpha$), 169.0 ($-\text{CO}_2$)

e. 127.3, 128.6, 130.1 (phenyl), 152.0 (COCl)

f. Exact assignment not possible because of overlapping fluorene and phenyl signals.

4.2.1.2 X-ray Crystal Structure of 4.1

Crystals of 4.1 suitable for an X-ray structure determination were obtained from a hexane:toluene mixture (ca. 2:1) at -20°C . 4.1 crystallizes in the monoclinic system, $\text{P2}_1/\text{n}$ with 4 molecules per unit cell. An ORTEP plot of 4.1 is shown in Fig. 4.2. Bond lengths and bond angles are listed in Tables 24 and 25, respectively.

The BOCC-four-membered ring is not completely planar. This agrees with the result obtained for the cycloadduct of $\text{tmpB}=\text{CR}_2$ and diphenylketone 4a (see eq. 4.1a)²⁾.

The B-C bond length of 1.634(4) Å is quite long even longer than in 4a (1.624(5)Å), while the B-N bond length, of 1.403(4) Å is identical to that found in 4a (1.404(5)Å). The C-C8 bond length, on the other hand, is slightly shorter than that found in the benzophenone adduct (ca. 3 pm), whereas the C8-O bond length is slightly longer (ca. 3 pm). The lengths of these bonds, however, definitely imply a significant amount of steric crowding caused by the presence of tmp, fluorene and $\text{CpFe}(\text{CO})_2$, all attached to a four-membered ring.

The bond angles in the four-membered ring of 4.1 are nearly identical ($\pm 1^\circ$) to the corresponding bond angles in 4a.

Table 24: Selected Bond Lengths (in Å) in 4.1. The atoms are numbered as in the ORTEP Plot (Fig. 4.2)

Fe	-C(1)	2.116(4)	Fe	-C(2)	2.125(2)
Fe	-C(3)	2.120(4)	Fe	-C(8)	2.079(3)
C(1)	-C(2)	1.424(5)	C(1)	-C(5)	1.396(5)
C(6)	-O(6)	1.146(4)	C(7)	-O(7)	1.149(5)
C(8)	-C(9)	1.520(4)	C(8)	-O	1.489(3)
C(8)	-C	1.582(4)	O	-B	1.403(4)
B	-N(1)	1.403(4)	B	-C	1.634(4)
N(1)	-C(10)	1.521(4)	N(1)	-C(14)	1.508(4)
C	-C(20)	1.514(4)	C	-C(31)	1.533(4)

Table 25: Selected Bond Angles (in degrees) in 4.1. The atoms are numbered as in the ORTEP Plot (Fig. 4.2)

C(1)	-Fe	-C(2)	39.2(1)	C(2)	-Fe	-C(4)	65.2(1)
C(1)	-Fe	-C(6)	159.9(2)	C(2)	-Fe	-C(6)	124.1(2)
C(1)	-Fe	-C(8)	106.7(1)	C(2)	-Fe	-C(8)	146.0(1)
C(5)	-Fe	-C(8)	87.2(1)	Fe	-C(6)	-O(6)	176.5(3)
Fe	-C(7)	-O(7)	172.4(3)	Fe	-C(8)	-C(9)	108.8(2)
Fe	-C(8)	-O	115.0(2)	C(9)	-C(8)	-O	105.5(2)
Fe	-C(8)	-C	122.0(2)	C(9)	-C(8)	-C	112.1(2)
O	-C(8)	-C	91.5(2)	C(8)	-O	-B	91.9(2)
O	-B	-N(1)	127.4(3)	O	-B	-C	92.5(2)
N(1)	-B	-C	139.9(3)	B	-N(1)	-C(10)	117.8(2)
B	-N(1)	-C(14)	119.5(2)	C(10)	-N(1)	-C(14)	120.3(2)
C(8)	-C	-B	80.6(2)	B	-C	-C(20)	134.4(2)
B	-C	-C(31)	105.3(2)	N(1)	-C(10)	-C(11)	111.9(2)

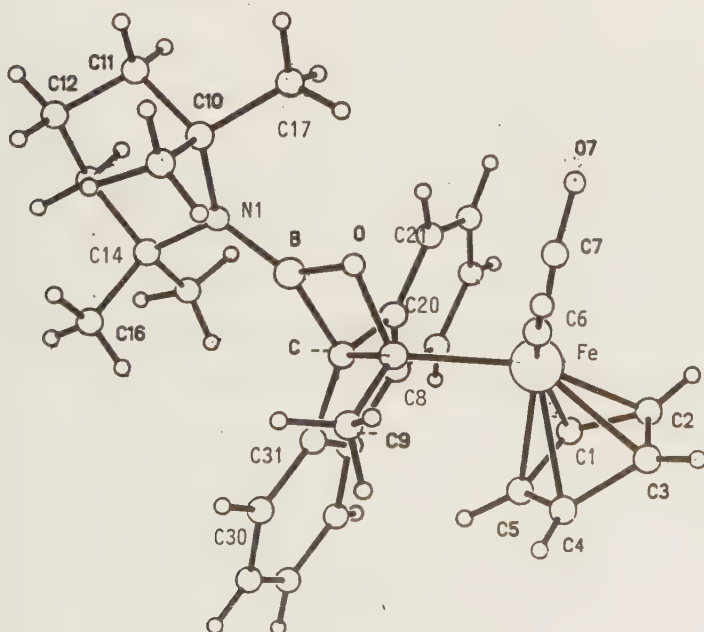
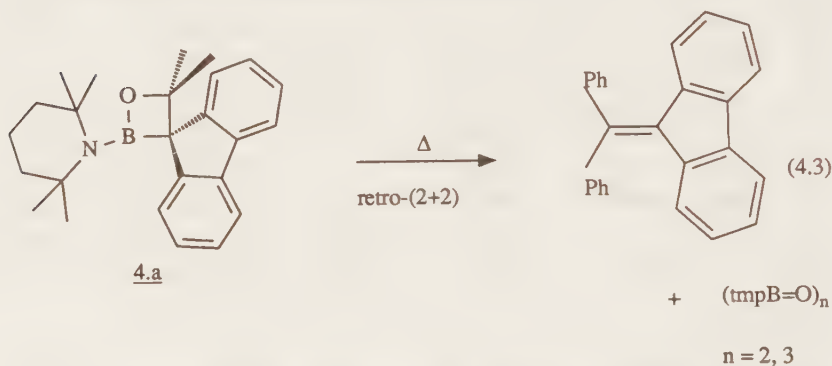


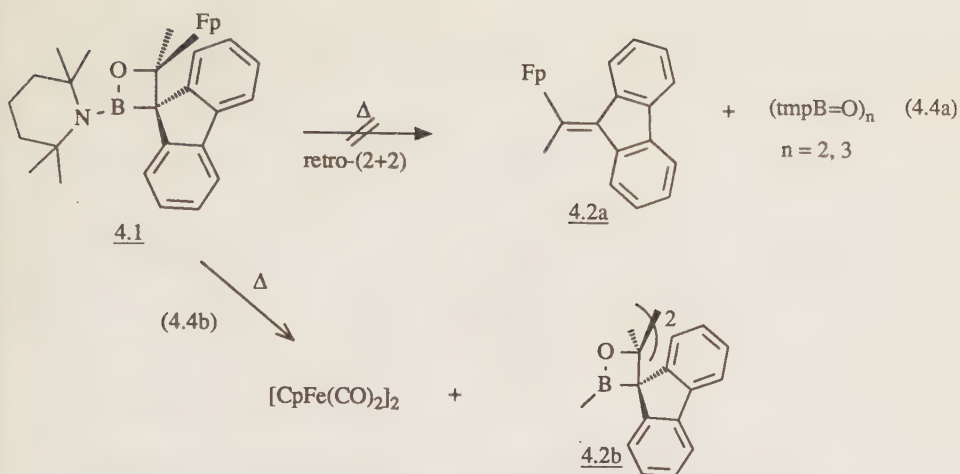
Fig. 4.2: ORTEP Plot of 4.1.

4.2.1.3 Thermolysis of 4.1

The product formed by the addition of benzophenone to $\text{tmpB}=\text{CR}_2$ decomposes at $>250^\circ\text{C}$ via a (2+2) cycloreversion to yield dimeric and trimeric ($\text{tmpB}=\text{O}$) and the corresponding alkene⁽²⁾ (eq.4.3).

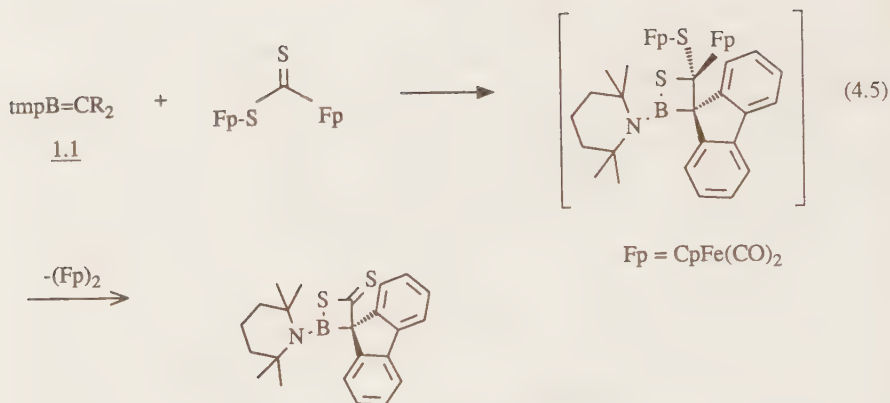


In an analogous fashion, 4.1 was expected to undergo a *retro*-(2+2) addition to yield $(\text{tmpB}=\text{O})_n$ and the corresponding (vinyl) $\text{Fe}(\text{CO})_2\text{Cp}$ (4.2a, eq. 4.4a), which, it was thought, might undergo additional loss of CO to yield higher intramolecular coordination. In fact, however, no CO was found to be eliminated (Töpler-pump measurement, $T = 130^\circ\text{C}$) and the ^{11}B -NMR signal did not change significantly. A red-green product sublimed out of the reaction mixture and could be identified as the stable, readily sublimable dimer $(\text{CpFe}(\text{CO})_2)_2$. Thus, whereas purely organic oxaboretanes undergo cycloreversion determined by the thermodynamic stability of the resulting boroxanes, in the adduct 4.1, the Fe-C9 bond is cleaved first, thus resulting in elimination of (Fp) (eq. 4.4b). It will be recalled that, in the mass spectrum of 4.1, the peak of greatest intensity corresponded to the $(\text{M}-(\text{CpFe}(\text{CO})_2))^+$ fragment, thus demonstrating the lability of the Fe-C σ -bond in the iron-alkyl (see section 4.2.1).



4.2.2 Reaction with $(\text{CpFe(CO)}_2)_2\text{CS}_2$

Because of the ease with which tmpB=CR_2 reacted with $\text{CpFe(CO)}_2\text{COCH}_3$ and with the thioketone, adamantanethione³⁾, the reaction with the bis(Fp)thioester was attempted in the hope of generating a thioborethane. In fact, reaction does occur within hours. A single boron-containing product ($\delta^{11}\text{B} = 44$ ppm) is produced, but work-up results in the isolation of two products (as in eq. 4.5), one being $(\text{CpFe(CO)}_2)_2$ ⁵⁾, the other was characterized by analysis, I.R. and NMR as 4.3.



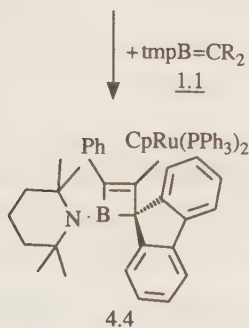
4.3

All data (¹H, ¹³C, ¹¹B) agree with the cycloaddition product from tmpB=CR₂ and CS₂⁷⁾ (see Tables 21-23).

4.3 Reaction of tmpB=CR₂ with (Cyclopentadienyl)bis(triphenylphosphine) ruthenium(phenyl-acetylide)

Reactions of tmpB=CR₂ with substituted acetylenes have been found to lead rapidly to the formation of stable (2+2) cycloaddition products when the acetylenes are substituted with polarizing groups such as NEt₂²⁾ or NMe₂⁸⁾. However, non-polar acetylenes such as HC≡C-CMe₃ have been shown to react very slowly, if at all, to the desired cycloaddition products. It was, nonetheless, hoped that the transition metal complex CpRu(PPh₃)₂C≡CPh would prove to be reactive enough to lead to the formation of cycloadduct, 4.4. Assuming the presence of polarity, due to the resonance form (b), reaction should proceed as shown in eq. 4.6.

Indeed, after stirring the reactants for 2 weeks at room temperature, a signal at δ¹¹B = 33.3 ppm could be detected. However, stirring for an additional several weeks did not bring about further reaction and all attempts at isolating the assumed



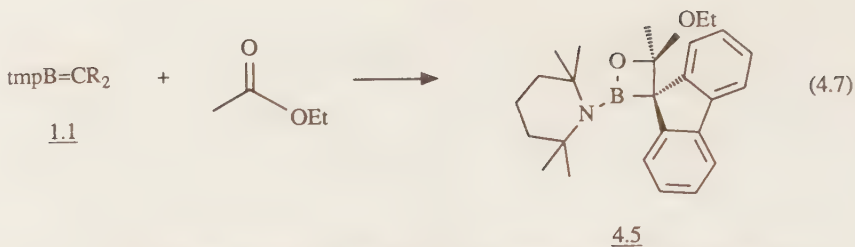
product 4.4 resulted in the retrieval of small amounts of tmpB=CR₂. The reason for the very slow reaction could be steric in nature (ie. with the two bulky PPh₃ groups). However, reactions with other, less bulky transition metal acetylides were not investigated in the course of this research.

4.4 Reactions of tmpB=CR₂ with Organic Esters, Amino Acids, Acid Chlorides, and Carbene Complexes

4.4.1 Reaction with Acetic Acid Ethyl Ester

tmpB=CR₂ and (EtO)COCH₃ react rapidly at room temperature (eq. 4.7) to yield the cycloadduct 4.5 as a colorless solid, characterized by analysis, I.R., and NMR (see above, Tables 21-23).

The I.R. spectrum indicates the lack of absorptions between 1480 and 2850 cm⁻¹. Thus, both ν(N=B=C) and ν(C=O) have disappeared, implying that the cycloaddition and not the migration of OEt has occurred (4.5a). Furthermore, the ¹¹B-NMR signal at δ¹¹B = 36.1 ppm clearly corresponds to the oxaboretane, 4.5.

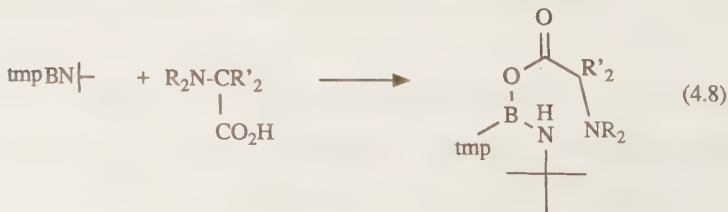


The ^1H -NMR spectrum indicates free rotation about the B-N bond. The methyl protons from the tmp ring fall close to those from the ester at $\delta^1\text{H} = 1.25\text{--}1.68$ ppm. The methylene protons from the ethyl ester function are diastereotopic ($\delta^1\text{H} = 3.10$ and 3.52 ppm). Each signal integrates to 1H and each consists of overlapping doublets of quartets. The geminal coupling constant $J_{\text{gem}}(^1\text{H}\text{--}^1\text{H})$ is 30 Hz.

The ^{11}B -NMR spectrum in CDCl_3 indicates a slight amount of association between the boron atom and the ketone function. A signal is found at $\delta^{11}\text{B} = 18.5$ ppm with 20% of the intensity of the main signal at $\delta^{11}\text{B} = 36.1$ ppm. The spectrum measured at slightly increased temperature (30°C) contains only one signal at $\delta^{11}\text{B} = 35.9$ ppm.

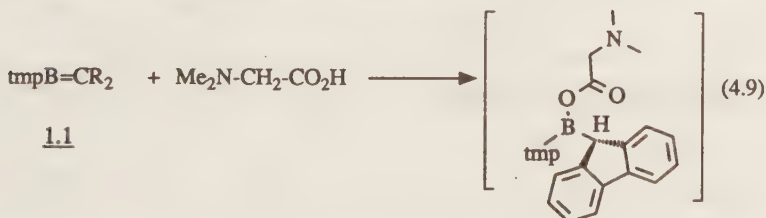
4.4.2 Reaction with N,N-Dimethylglycine

G.Geisberger⁹⁾ demonstrated the utility of the amino-imino-borane $\text{tmpB}\equiv\text{N}^t\text{Bu}$ as a building block for boron-containing amino acid derivatives. Addition of N,N-dialkyl-amino acids, results in the rapid addition of the carboxylic acid function but not the C=O group across the $\text{B}\equiv\text{N}$ bond (eq. 4.8).

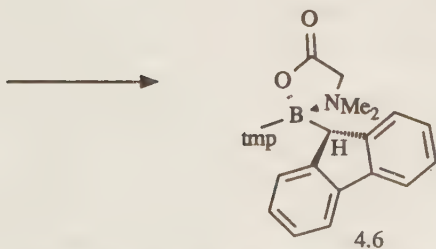


Such compounds should be stable in water for a long enough period so as to allow their use as neutron acceptors in radiation therapy. The synthesis of a boron-rich amino-imino-borane, followed by reaction with amino acids, should result in compounds which would be therapeutically useful. The compounds would first be enriched with ^{10}B and then, following their injection into the body, bombarded with slow neutrons to yield the unstable (^{11}B)* which decomposes to ^4He and ^7Li in a reaction which gives off a large amount of energy. This reaction has a radius of effect of only $10\text{ }\mu\text{m}$, which corresponds roughly to the diameter of a cell¹⁰⁾ and can be used to specifically destroy tumor cells.

In the search for potential water-stable boranes, $\text{tmpB}=\text{CR}_2$ was reacted with N,N -dimethylglycine⁹⁾. The reaction proceeded smoothly at -35°C (according to eq. 4.9) to yield 4.6 as a stable product.



4.6a (not observed)



4.6

The insertion into the O-H bond is clearly much faster than the (2+2) cycloaddition across the C=O bond. The intermediate 4.6a is not observed, nor could it be observed in an ^{11}B -NMR spectrum at 93°C . Only 4-coordinate boron ($\delta^{11}\text{B} = 6.1\text{ ppm}$) is found, corresponding to the adduct 4.6. Furthermore, $\nu(\text{C}=\text{O})$ is observed in the I.R. spectrum at 1735 cm^{-1} . All NMR data are listed in Tables 21-23 (see above).

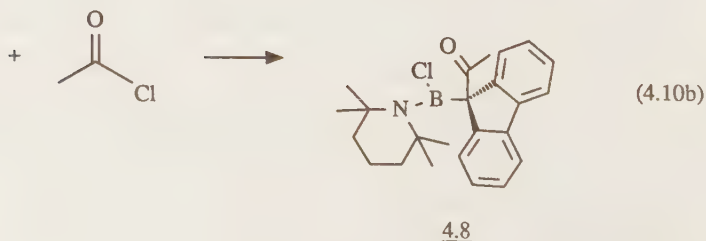
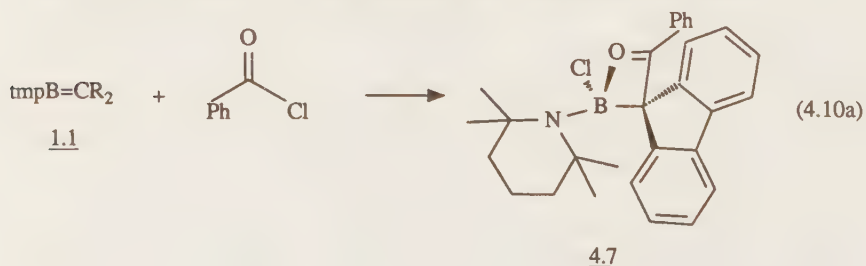
That the NMe_2 and not the $\text{C}=\text{O}$ function coordinates to the boron atom is

demonstrated by the inequivalence of the methyl groups of the NMe_2 function at $\delta^1\text{H} = 2.57$ and 2.35 ppm. In the ^{13}C -NMR spectrum the corresponding C-atoms are found at $\delta^{13}\text{C} = 61.9$ and 55.1 ppm.

The tmp region of the ^{13}C -NMR spectrum reveals two interesting structural features. The coordination of the NMe_2 group to the B-atom excludes B-N back-bonding between the tmp N-atom and the B-atom. This is evidenced by a 13 ppm high-field shift for the quaternary C-atoms (C2,6: $\delta^{13}\text{C} = 44.6$ ppm) relative to three-coordinate adducts of $\text{tmpB}=\text{CR}_2$. The ^{13}C -NMR spectrum also indicates a lack of symmetry at the boron center (the boron atom is chiral) and, hence, non-equivalence of the tmp methyl groups, C7/8 and C7'/8', because of diastereotopism ($\delta^{13}\text{C} = 36.7$ ppm and 28.0 ppm). The remaining tmp and fluorene signals do not present any unusual features.

4.4.3 Reactions with Acid Chlorides

$\text{tmpB}=\text{CR}_2$ reacts with benzoyl and acetyl chloride at room temperature to the two new compounds, 4.7 and 4.8, respectively (according to eq. 4.10a,b).



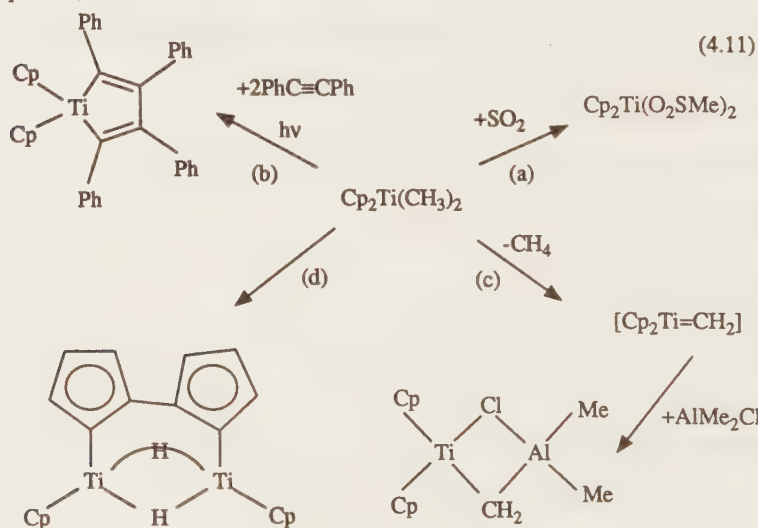
4.7 is a stable colorless solid, which could be characterized by analysis and NMR (see above, Tables 21-23); however, 4.8 could only be observed in solution. Though $\text{tmpB}=\text{CR}_2$ and CH_3COCl did react, it required several days' stirring at room temperature and an excess of the acid chloride. The ^{11}B -NMR signal at $\delta^{11}\text{B} = 42.4$ ppm corresponds to a chloro(organyl)(tmp)borane. Attempts to isolate a product by crystallization failed.

4.7 possesses a ^{11}B -NMR signal at $\delta^{11}\text{B} = 27.3$ ppm, far upfield from other oxaboretanes. The most probable reason for this high-field shift is a significant interaction between the B- and Cl-atoms. This is borne out by the high-field position of the quaternary C-atoms (C2,6) in the tmp ring ($\delta^{13}\text{C} = 54.5$ ppm). In 4.7, the interaction between B and Cl is certainly weaker than that between B and NMe_2 found in 4.6. Thus, in 4.7, C2 and C6 are found a few ppm further upfield than usual, whereas in 4.6, the upfield shift is greater than 10 ppm.

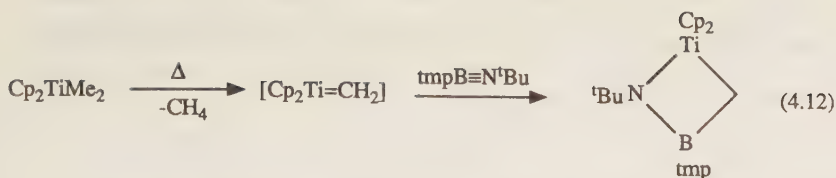
The lack of symmetry at the C-atom attached to C9 is made apparent by the partial splitting of the ^{13}C -NMR signals in the fluorene region into two sets of six. C10 and C10' are found at $\delta^{13}\text{C} = 139.1$ and 139.5 ppm; C15 and C15' are represented by signals at $\delta^{13}\text{C} = 137.4$ and 137.6 ppm. The two lower-field benzene-like C-atoms ($\delta^{13}\text{C} = 130.1$ and 129.3 ppm) can be assigned with reasonable certainty to C1 and C4 of the phenyl ring. The other ^{13}C -NMR signals fall too close together for an unambiguous assignment to be made. The carbonyl carbon in the starting material ($\delta^{13}\text{C} = 168.5$ ppm) has moved to $\delta^{13}\text{C} = 152.0$ ppm in 4.7. This is not surprising since, though the formal hybridization has been changed, the C-atom is still bound to three strongly electron-withdrawing substituents. Such a low-field shift is, thus, to be expected⁵⁾.

4.4.4 Reaction with Dimethyltitanocene

Compounds of titanium are of importance in alkene polymerization reactions as components of Ziegler-Natta catalyst systems¹¹⁾. Metallacyclobutane complexes have been postulated as the reactive intermediates in such processes¹²⁾. Dimethyltitanocene undergoes insertion reactions (eq.4.11a) into the Ti-Me-bond¹³⁾, as well as photochemical elimination of the Me-groups (eq. 4.11b)¹⁴⁾. The thermal decomposition either in the solid state¹⁵⁾ or in inert solvents¹⁶⁾ leads to the formation of the fulvalene dimer with loss of methane gas (eq. 4.11d).

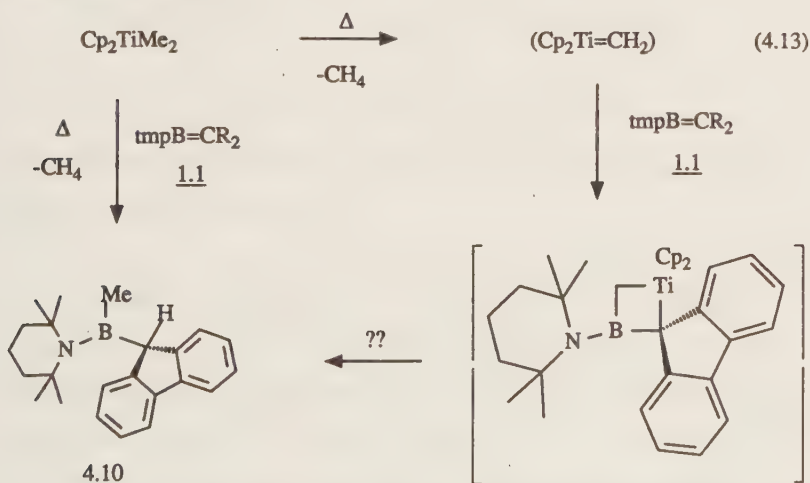


Many authors suggest that the intermediate in the thermal decomposition reaction is the carbene (or "alkylidene") species $\text{Cp}_2\text{Ti}=\text{CH}_2$ ^{16),17)}. Such a species can be stabilized by Me_2AlCl as "Tebbe's Reagent"¹⁸⁾. Reactions in which this intermediate is trapped by "true" cycloaddition reactions were unknown until 1986. At that time, Nöth and Wietelmann¹⁹⁾ reported the isolation of the four-membered heterocyclic ring system $\text{Cp}_2\text{Ti}-\text{CH}_2-\text{B}(\text{tmp})-\text{N}^t\text{Bu}$, formed according to eq. 4.12.



Pactzold. *et al.* investigated a similar system (${}^t\text{BuB}\equiv\text{N}^t\text{Bu}$) at approximately the same time²⁰).

Because of the demonstrated polarity of this "nucleophilic" or "Schrock" carbene ($\text{Cp}_2\text{Ti}^{\delta+}=\text{CH}_2^{\delta-}$)²¹), it was hoped that reaction with $\text{tmpB}=\text{CR}_2$ would lead to the 1,3-metalla-bora-cyclobutane, 4.9. However, the compound 4.10 is isolated instead, the effective product of the addition reaction of CH_4 across the $\text{B}=\text{C}$ double bond (eq.4.13).



4.10 could be isolated only in poor yield, but its structure is clearly inferred from the spectroscopic data ($\delta^{11}\text{B} = 49.5$ ppm; $\delta^1\text{H}$: $\text{CH}_3\text{-B}$ at 0.04 ppm; C9-H at 4.63 ppm; $\delta^{13}\text{C}$: two boron-bound C-atoms at 33.1 ppm and 50.2 ppm; other data listed in the experimental section, Experiment 4.8). The path of formation of 4.10 must remain an open question. However, it should be mentioned that, although several authors have concluded that $(\text{Cp}_2\text{Ti}=\text{CH}_2)$ is the major intermediate involved in the decomposition of Cp_2TiMe_2 , they also mention the ease with which H-atoms are abstracted either from the methyl groups or from the Cp rings¹⁶).

Thus, the desired ring compound 4.9 may be formed, followed by H-atom abstraction from further equivalents of Cp_2TiMe_2 , or from its decomposition products to yield 4.10.

Chapter 5:

Reaction of $\text{tmpB}=\text{CR}_2$ with Transition Metal Carbonyl Complexes: Transition Metal Alkylidene Boranes

5.1 Introduction

Compounds containing transition metal-boron bonds can be divided into three general classes¹⁾:

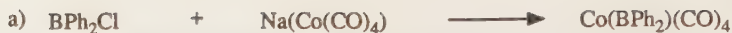
a) transition metal complex- BX_3 Lewis base-acid interactions;

b) transition metal-borohydride complexes, such as tetrahydroborates, metalla-boranes, and -carboranes, in which the bonds between the metal and boron atoms are generally hydride bridged;

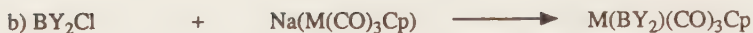
c) transition metal-boryl complexes, which contain single ($\text{M}-\text{BX}_2$) units and, thus, metal-boron σ -bonds. Though this latter class of compounds is at first sight fully analogous to transition metal-alkyl complexes, their instability has been noted by many authors^{1),2)}. It is most likely for this reason that no transition metal-boryl has yet been characterized X-ray structural determination. Compounds containing bonds between transition metals and boron whose structures been unequivocally proven by X-ray crystallography are all conspicuously confined to the higher boranes and carbaboranes or to aromatic ring systems containing boron atoms (such as borabenzene)¹⁾.

Three routes have generally been used to obtain transition metal-boryls:

1) The reaction of boron halides with transition metal carbonylates:



Lit: 2, 3

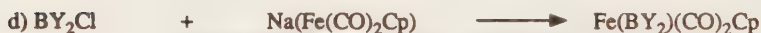


$\text{M} = \text{Mo}, \text{W}; \text{Y} = \text{Ph}, \text{Cl}$

Lit: 4



$\text{Y} = \text{Cl}, \text{R}, \text{NR}_2; \text{L} = \text{CO}, \text{PR}_3$ Lit: 5, 6



$\text{Y} = \text{Ph}, \text{NEt}_2, \text{Cl}$

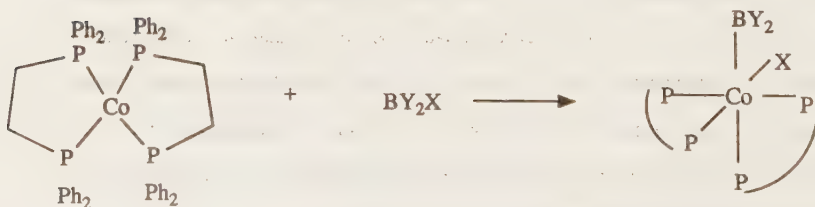
Lit: 7, 8

2) Disproportionation with H_2 -elimination:



Lit: 9 - 10

3) Oxidative addition reactions of boron halides:



$\text{Y} = \text{Ph}; \text{X} = \text{Cl}$ Lit: 11

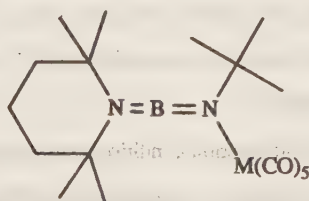
The oxidative addition between catecholborane and Wilkinson's catalyst, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, could be proven by I.R.¹²⁾ and characterized by NMR¹³⁾, but no

crystal structure has been reported. The oxidative addition product has furthermore been implicated in the $(\text{Rh}(\text{PPh}_3)_3\text{Cl})$ -catalyzed hydroboration of olefins and alkynes¹³⁾.

Another possible route to M-B bonds (M = transition metal) would involve the replacement of olefins, carbonyls or some other labile ligand L in a transition metal complex by B=E (E = N, C) multiple-bond units to yield η^2 - "side-on"-bound complexes (eq. 5.1).



Though many transition metal complexes of alkyl-imino- and amino-imino-boranes are known, no example of side-on coordination has been found^{14),15)}. All are bound *via* the lone pair of the imino-N-atom as in:



$\text{M} = \text{Cr}, \text{W}$ Lit: 14

The reason for this behavior most likely lies in the strongly polarized B-N bond and in the donor capacity of substituted amines and imines *via* their nitrogen lone pair. A methylene-borane, on the other hand, is much less polarized and has much weaker donor properties. It should behave much more like a "normal" asymmetric olefin. Analogy was drawn in section 1.3 between the reactivity of electrophilic olefins such as $\text{CF}_2=\text{CF}_2$ and the amino-fluorenylidene-borane in their reactions with arsenic trihalides. In this chapter, this analogy will be further explored with respect to transition metal-olefin complexes.

5.2 Reaction of $\text{tmpB}=\text{CR}_2$ with $\text{Fe}_7(\text{CO})_9$

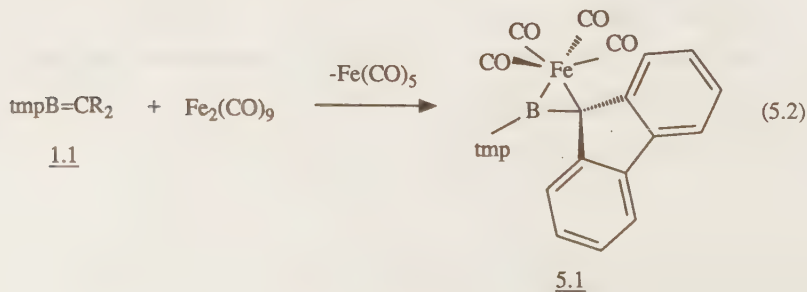
The synthesis of the first $\text{Fe}(\text{CO})_4$ (olefin) complex was reported in 1960 by Kettle and Orgel¹⁷. They obtained $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHCN})$ in 2% yield from the reaction of $\text{Fe}_2(\text{CO})_9$ in boiling acrylonitrile. Its crystal structure was described in 1961¹⁷. Since then, many analogous compounds have been reported.

Synthetic methods for preparing compounds of the type $\text{Fe}(\text{CO})_4(\eta^2\text{-hydrocarbon})$ are few and simple. In general, two methods are employed¹⁸⁾:

a) From $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ and an olefin. Mono-olefin complexes of $\text{Fe}(\text{CO})_4$ are formed by direct reaction in organic solvents at room temperature. $\text{Fe}(\text{CO})_5$ is eliminated when $\text{Fe}_2(\text{CO})_9$ is used, but is easily removed *in vacuo*.

b) Photolysis of $\text{Fe}(\text{CO})_5$ in the presence of an olefin. This method has also found wide use, in particular because of the low cost of $\text{Fe}(\text{CO})_5$. An excess of $\text{Fe}(\text{CO})_5$ may be used and removed later *in vacuo*. The disadvantage of this method is the possible loss of two equivalents of CO to yield a mixture of the mono- and di-olefin species¹⁹).

Because of the mild reaction conditions and ready availability of $\text{Fe}_2(\text{CO})_9$, this was the method of choice for reaction with $\text{tmpB}=\text{CR}_2$. Stirring equimolar amounts of the two compounds in toluene at room temperature for 12 h results in a dark red-green solution from which $\text{Fe}(\text{CO})_5$ is removed *in vacuo*. A stable crystalline product could be isolated from toluene:hexane at low temperature, which was characterized by analysis, I.R., NMR, and X-ray crystallography as 5.1. The formation of this compound is depicted in eq. 5.2.



5.2.1 Spectroscopic Data

The ^{11}B -NMR spectrum of 5.1 in C_6D_6 contains one signal at $\delta^{11}\text{B} = 58.5$ ppm. This represents no significant change from the starting material ($\delta^{11}\text{B} = 59.2$ ppm²¹). However, the peak half-width is reduced by nearly 300 Hz, indicating a different environment at the boron atom.

The ^1H -NMR spectrum clearly proves the presence of a new compound. Whereas the tmp ring protons in $\text{tmpB}=\text{CR}_2$ are found between $\delta^1\text{H} = 1.51$ and 1.77 ppm²¹), they lie over a much larger range in 5.1: $\delta^1\text{H} = 0.80$ to 1.81 ppm. Furthermore, two sharp singlets, each integrating to 6H, are found at $\delta^1\text{H} = 0.80$ and 1.81 ppm, for the tmp methyl groups. Thus, the symmetry of the starting $\text{tmpB}=\text{CR}_2$ is lost, in which only one signal for the 4 methyl groups was found ($\delta^1\text{H} = 1.51$ ppm²¹).

The ^{13}C -NMR spectrum indicates the loss of symmetry parallel to the fluorene plane. 7 different signals are found in the aliphatic region for the tmp C-atoms. They are, furthermore, all shifted to relatively low field implying a significant loss of electron density, most likely through a strong B-N ($p\pi-p\pi$) interaction. The ^{13}C -NMR data for 5.1 are listed in Table 28 with those of the starting material.

Another interesting feature of the ^{13}C -NMR spectrum is the presence of only 6 signals for the 12 C-atoms of the fluorenyl ring system, implying the presence of a symmetry plane perpendicular to the fluorenyl ligand. As in the tmp ring, these signals are found at extremely low field relative to the starting fluorenylidene borane. C10 lies at $\delta^{13}\text{C} = 153.4$ ppm: this represents a downfield shift of 9.3 ppm relative to $\text{tmpB}=\text{CR}_2$. C15 lies at $\delta^{13}\text{C} = 138.4$ ppm, representing a downfield shift of 4.7 ppm.

That C9 is directly bound to iron is evidenced by its high-field ^{13}C -NMR signal at $\delta^{13}\text{C} = 27.8$ ppm, a position typical for olefinic carbon atoms bound directly to first-row transition metals²⁰. The other ^{13}C -NMR signals are shifted

much less implying largely through-bond effects for the downfield shifts. These effects taper off with increasing distance from the Fe-bound C-atom (C9).

At room temperature, only one ^{13}C -NMR signal is found for the carbonyl ligands. However, upon cooling the sample to 231K, three signals appear at $\delta^{13}\text{C} = 209.4, 207.8, \text{ and } 206.6$ ppm, of relative intensity 1:1:2, respectively. This finding supports the presence of an $\text{Fe}(\text{CO})_4$ unit in which two CO ligands are equivalent by symmetry. This fact is further supported by the I.R. spectrum, in which three strong absorptions are found at 2064, 2011, and 1962 cm^{-1} . A slight shoulder is attached to the 1962 cm^{-1} band at 1971 cm^{-1} .

The final spectroscopic proof that the B=C unit is coordinated to $\text{Fe}(\text{CO})_4$ comes from the I.R. spectrum as well: the absorption at 1717 cm^{-1} , attributed to $\nu(\text{N}=\text{B}=\text{C})$ in $\text{tmpB}=\text{CR}_2^{21}$, has disappeared. The region between 1600 and 1962 cm^{-1} is free of absorptions.

The NMR data of 5.1 are listed in Tables 26-28. The I.R. data of the carbonyl region are listed in Table 29 (see also Fig. 5.1).

Table 26: ^{11}B -NMR Data of the Complexes 5.1-5.4 and the uncomplexed $\text{tmpB}=\text{CR}_2$, 1.1 (in ppm; half-widths in Hz; solvents numbered as in Table 1)

<u>Metal</u>				
<u>Fragment</u>	<u>Nr.</u>	<u>$\delta^{11}\text{B}$</u>	<u>$h_{1/2}$</u>	<u>Solvent</u>
$\text{Fe}(\text{CO})_4$	<u>5.1</u>	58.5	560	2
$\text{CpCo}(\text{CO})$	<u>5.2</u>	61.2	610	2
$\text{MeCpMn}(\text{CO})_2$	<u>5.3</u>	58.0	560	2
$(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_2$	<u>5.4</u>	57.2	500	2
----	<u>1.1^a</u>	59.2	800	2

a. Lit.: 21

Table 27: ^1H -NMR Data of the Complexes 5.1-5.4 and of the uncomplexed $\text{tmpB}=\text{CR}_2$, 1.1 (in ppm; solvents as in Table 26)

<u>Metal</u> <u>Fragment</u>	<u>Nr.</u>	<u>CH₃</u> (tmp)	<u>CH₂</u> (tmp)	<u>arom. H</u> (fluorene)	<u>other</u>
----	<u>1.1</u> ^a	1.51	1.64-1.77	7.16 7.27 7.57 7.96(each 2H)	--
$\text{Fe}(\text{CO})_4$	<u>5.1</u>	0.80 1.80	1.33	7.15-7.74	--
$\text{CpCo}(\text{CO})$	<u>5.2</u>	0.76 2.09 2.37	1.50-1.57 1.72-1.82	7.19-7.23(6H) 7.80-7.86(2H)	4.56 (Cp)
$\text{MeCpMn}(\text{CO})_2$	<u>5.3</u>	0.61, 1.66, 2.01 (21H, tmp and CH_3Cp)		7.10-7.23(6H) 7.80-7.86(2H)	3.63 3.90 (b)
$(\text{C}_6\text{H}_6)\text{Cr}$ $(\text{CO})_2$	<u>5.4</u>	0.75 2.16	1.12-1.49	7.06-7.60(6H) 7.91-8.02(2H)	3.81 3.99 (c)

a. Lit.: 21.

b. each signal integrates to 2H; $\text{C}_4\text{H}_4\text{CMe} = \text{Cp}'$.

c. each signal integrates to 3H; C_6H_6 .

Table 28: ^{13}C -NMR Data of the Complexes 5.1-5.4 and of the uncomplexed $\text{tmpB}=\text{CR}_2$, 1.1 (in ppm; solvents as in Table 26; numbering scheme as in Fig. 1.1)

Table 28a: ^{13}C -Resonances of the tmp ring

<u>Nr.</u>	<u>C4</u>	<u>C7/8</u>	<u>C3/5</u>	<u>C2/6</u>	<u>other</u>
<u>1.1</u> ^a	16.7	32.9	38.0	56.6	---
<u>5.1</u>	16.3	33.2 34.3	38.6 39.2	58.7 61.8	b
<u>5.2</u>	16.7	31.5 33.5 34.2 37.1	39.1 39.7	56.8 59.9	c
<u>5.3</u>	15.7	32.9	38.6 39.5	59.0 63.3	d
<u>5.4</u>	15.8	32.7 33.2	38.6 39.7	59.7 63.3	e

a. Lit. 21

b. 208.7 ($\underline{\text{CO}}$); at $T = 230\text{K}$, $\delta^{13}\text{C} = 209.4, 207.8, 206.6$ (rel. intensities: 1:1:2).

c. 89.2 (Cp), 205.1 ($\underline{\text{CO}}$)

d. 12.9 ($\underline{\text{CH}_3\text{Cp}}$); 89.8, 90.9 ($\underline{\text{C}_4\text{H}_4\text{CMe}}$); 101.9 ($\text{C}_4\text{H}_4\underline{\text{CMe}}$); 230.5 ($\underline{\text{CO}}$)

e. 97.8, 100.0, 104.3 ($\underline{\text{C}_6\text{H}_6}$); 187.6, 188.2 ($\underline{\text{CO}}$)

Table 28b: ^{13}C -Resonances of the fluorene ring

<u>Nr.</u>	<u>C9</u>	<u>C10</u>	<u>C15</u>	<u>C11</u>	<u>C12</u>	<u>C13</u>	<u>C14</u>
<u>1.1</u> ^a	83.2	144.1	133.7	121.0	124.8	120.9	119.8
<u>5.1</u>	27.8	153.4	138.4	123.6	124.9	126.3	121.0
<u>5.2</u>	21.7	155.9	137.6	122.8	124.9	124.2	120.5
		157.4	138.0	123.1	126.3	124.4	120.7
<u>5.3</u>	24.2	158.4	136.3	122.0	124.5	125.0	119.8
<u>5.4</u>	26.2	162.9	135.1	121.2	124.3	125.1	120.3
		163.1	135.2				

a. Lit.: 21.

Table 29: CO Bands from the Infrared Spectra of the Complexes 5.1-5.4 (in cm^{-1} ; all spectra were recorded in CCl_4)

<u>Metal</u> <u>Fragment</u>	<u>Nr.</u>	<u>$\nu(\text{C}\equiv\text{O})$</u>
$\text{Fe}(\text{CO})_4$	<u>5.1</u>	2064 2011 1971 (shoulder) 1962
$\text{CpCo}(\text{CO})$	<u>5.2</u>	1958
$\text{MeCpMn}(\text{CO})_2$	<u>5.3</u>	1937 1876
$(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_2$	<u>5.4</u>	1889 1841

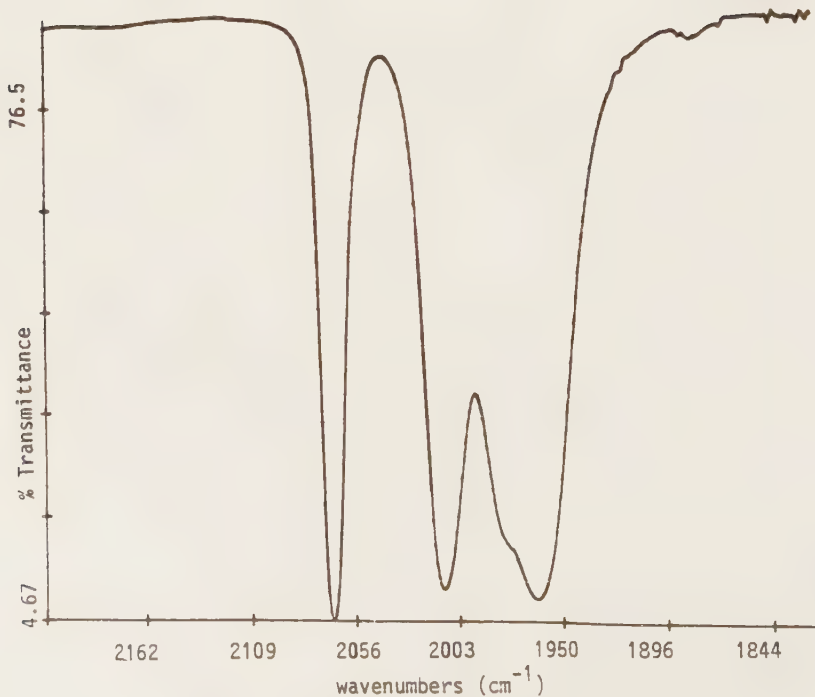


Fig. 5.1: CO Region of the I.R. Spectrum of 5.1

5.2.2 X-ray Crystal Structure of 5.1

An ORTEP plot of the molecule is depicted in Fig. 5.2. Selected bond lengths and angles are listed in Tables 30 and 31.

The B-C bond occupies an equatorial position of a distorted trigonal bipyramid formed by the CO ligands surrounding the Fe atom. The bulky ligand $\text{tmpB}=\text{CR}_2$ forces the bond angle between the axial carbonyls to be much smaller than the 180° found in $\text{Fe}(\text{CO})_5$: $\text{C}_{\text{ax}}\text{-Fe-C}_{\text{ax}} = 151.2(2)$.

The B-C bond length has increased in 5.1 by $0.1 \text{ \AA}$ relative to the non-complexed ligand. The B-N bond length of $1.377(6) \text{ \AA}$ indicates significant double-bond character, as was already deduced from the ^1H - and ^{13}C -NMR spectra. The C_2N -plane of the tmp ring is almost perfectly parallel to the Fe-B-C-plane (the angle between the two normals to the planes is 4.7°).

That the B-C unit is found in equatorial position and not parallel to the axial CO-ligands is typical for $\text{Fe}(\text{CO})_4(\eta^2\text{-hydrocarbon})$ complexes. This configuration allows for a greater degree of metal-ligand ($d\pi\text{-}p\pi$) overlap. Axial coordination is only found for ligands which can serve as significant σ -donors (phosphines, amines). Even in the bis(olefin)-complex $\text{Fe}(\text{CO})_3(\text{CH}_2=\text{CHCO}_2\text{Me})_2$, both olefins are in equatorial positions¹⁹⁾. On the other hand, in $\text{Fe}(\text{CO})_3(\text{PPh}_3)(\text{CH}_2=\text{CHCO}_2\text{Me})$, the phosphine ligand occupies an axial and the olefin an equatorial position²²⁾.

The lengthening of the B-C bond is typical of other analogous $\text{Fe}(\text{CO})_4(\eta^2\text{-heterocumulene})$ complexes. That the Fe-B bond ($2.125(5) \text{ \AA}$) is shorter than the Fe-C bond ($2.190(4) \text{ \AA}$) (in spite of the larger covalent radius of the boron atom) indicates that boron plays a dominating roll as a π -acceptor. This is in agreement with Floriani's²⁴⁾ finding that the stability of iron tetracarbonyl ($\eta^2\text{-heterocumulene}$) complexes is largely determined by the π -interaction between the C=X fragment (in our case, B=N) and the d-orbitals of the metal. Furthermore, viewing the boron atom as the more Lewis-acidic center, the Fe-B bond would be expected to be shorter because of the stronger back donation from the metal

orbitals. This same result is found when comparing the Fe-C bond lengths in $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_2)$ (2.12 Å) and $\text{Fe}(\text{CO})_4(\text{C}_2\text{F}_2)$ (1.99 Å)²⁶.

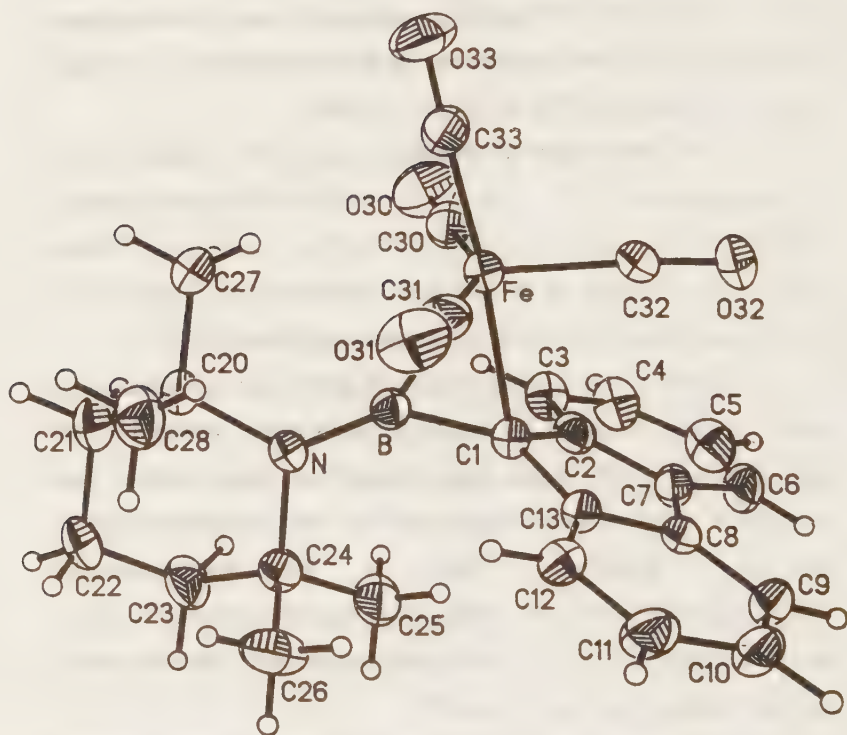


Fig. 5.2: ORTEP Plot of the compound 5.1

Table 30: Selected Bond Lengths (in Å) in 5.1. The atoms are numbered as in the ORTEP Plot (Fig. 5.2)

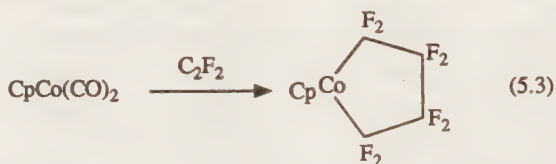
Fe	-C(30)	1.786(5)	Fe	-C(31)	1.786(5)
Fe	-C(32)	1.820(5)	Fe	-C(33)	1.820(5)
Fe	-B	2.125(5)	Fe	-C(1)	2.190(4)
C(30)	-O(30)	1.151(6)	C(31)	-O(31)	1.142(7)
C(32)	-O(32)	1.140(6)	C(33)	-O(33)	1.131(6)
N	-C(20)	1.530(6)	N	-C(24)	1.546(5)
N	-B	1.377(6)	C(20)	-C(21)	1.519(7)
C(20)	-C(27)	1.511(6)	C(20)	-C(28)	1.540(7)
C(21)	-C(22)	1.512(7)	C(22)	-C(23)	1.513(8)
C(23)	-C(24)	1.521(7)	C(24)	-C(25)	1.513(8)
C(24)	-C(26)	1.536(7)	B	-C(1)	1.518(7)
C(1)	-C(2)	1.496(6)	C(1)	-C(13)	1.499(6)
C(2)	-C(3)	1.389(7)	C(2)	-C(7)	1.411(6)
C(8)	-C(9)	1.406(7)	C(12)	-C(13)	1.382(6)

Table 31: Selected Bond Angles (in degrees) in 5.1. The atoms are numbered as in the ORTEP Plot (Fig. 5.2)

C(30)	-Fe	-C(31)	151.2(2)	C(30)	-Fe	-C(32)	104.5(2)
C(30)	-Fe	-C(33)	85.7(2)	C(31)	-Fe	-B	83.4(2)
C(31)	-Fe	-C(1)	93.4(2)	C(32)	-Fe	-C(33)	100.2(2)
C(32)	-Fe	-B	126.7(2)	C(32)	-Fe	-C(1)	85.5(2)
C(33)	-Fe	-C(1)	85.5(2)	C(33)	-Fe	-C(1)	174.3(2)
C(33)	-Fe	-B	133.2(2)	B	-Fe	-C(1)	41.2(2)
Fe	-B	-N	146.0(3)	Fe	-B	-C(1)	71.7(2)
N	-B	-C(1)	142.3(4)	C(13)	-C(1)	-C(2)	104.3(4)
Fe	-C(1)	-B	67.1(2)	Fe	-C(1)	-C(2)	111.3(3)
Fe	-C(1)	-C(13)	111.2(3)	C(1)	-C(2)	-C(3)	130.6(4)
C(3)	-C(2)	-C(7)	120.5(4)	C(3)	-C(4)	-C(5)	120.9(5)
C(4)	-C(5)	-C(6)	121.4(5)	C(7)	-C(8)	-C(9)	130.7(4)
C(9)	-C(8)	-C(13)	119.3(4)	C(1)	-C(13)	-C(8)	108.0(4)

5.3 Reaction of CpCo(CO)_2 with tmpB=CR_2

Though the (CpCo(CO)) fragment is isolobal with $(\text{Fe(CO)}_4)^{27}$, there are surprisingly few CpCo(CO) (mono-alkene) complexes known, and none has been characterized by X-ray crystallography. Reaction of CpCo(CO)_2 with C_2F_4 fails to yield the desired complex $\text{CpCo(CO)}(\eta^2\text{-C}_2\text{F}_2)$ but rather undergoes an oxidative coupling reaction to yield the octafluoro-cobalta-cyclopentane (eq. 5.3)²⁸.



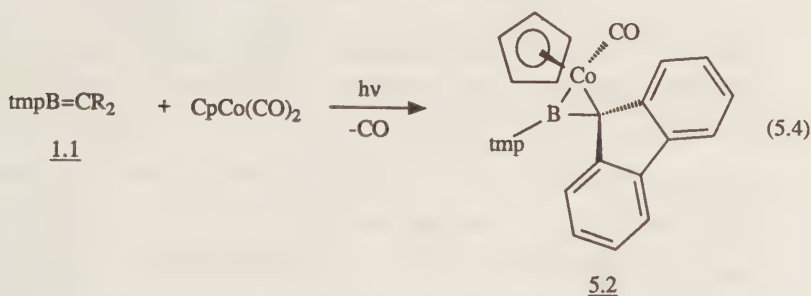
Mono-alkene complexes of Co(I) , when they do exist, are generally stabilized by phosphine ligands, as in $\text{CpCo(PPh}_3)(\eta^2\text{-C}_2\text{H}_2)^{29}$. Because the Fe(CO)_4 complex of tmpB=CR_2 had been found to be quite stable relative to other olefin complexes of Fe(CO)_4 , it was expected that reaction between tmpB=CR_2 and CpCo(CO)_2 might likewise yield a similarly stable complex.

5.3.1 Thermal Reaction

Heating CpCo(CO)_2 and tmpB=CR_2 in toluene for 12h led to a new boron-containing product ($\delta^{11}\text{B} = 36$ ppm). However, only a small amount of CO was observed to evolve and, when solvent was removed from the reaction mixture, a large amount of unreacted CpCo(CO)_2 was retrieved. All attempts to isolate the new product failed, and it must, therefore, be concluded that it was most likely the result of hydrolysis and oxidation.

5.3.2 Photolysis of CpCo(CO)_2 in the Presence of tmpB=CR_2

Photolysis of CpCo(CO)_2 in the presence of an equimolar amount of tmpB=CR_2 led to the formation of a new boron-containing product ($\delta^{11}\text{B} = 61.2$ ppm). Removal of solvent and unreacted CpCo(CO)_2 *in vacuo* followed by crystallization from hexane:toluene yielded a black solid which proved to be 5.2 formed according to eq. 5.4.



5.3.2.1 Spectroscopic Data

The spectroscopic data of 5.2 are given in Tables 26-29, above.

The I.R. spectrum of 5.2, like that of 5.1, contains no absorption at 1717 cm^{-1} , implying that the B=C unit is coordinated to the Co-center. A single strong absorption at $\nu = 1958\text{ cm}^{-1}$ indicates the presence of a mono-carbonyl fragment, as would be expected for 5.2. This is in contrast to the starting material CpCo(CO)_2 for which two strong bands at 2030 cm^{-1} and 1970 cm^{-1} are found³⁰. The low frequency shift to 1958 cm^{-1} of the remaining carbonyl indicates the poor π -acceptor ability of tmpB=CR_2 relative to CO.

The $^1\text{H-NMR}$ spectrum further supports the structure suggested for 5.2. As in 5.1, the tmp methyl resonances are split into at least two groups (exact assignments were difficult because of signal broadening from paramagnetic impurities) at $\delta^1\text{H} = 0.76\text{ ppm}$ and 2.09 ppm . The tmp region extends over 1.61

ppm, an area larger than in 5.1 and much larger than in $\text{tmpB}=\text{CR}_2$. This large splitting (at least 5 different signals could be identified, lying at intervals of 0.2 ppm, or further, apart) implies both hindered rotation about the B-N bond as well as a loss of symmetry relative to 5.1. This is to be expected since the cobalt center represents a center of asymmetry, being bound to Cp on one side and CO on the other. The symmetry plane perpendicular to the fluorene ring system is thus no longer present.

In the ^{13}C -NMR spectrum, 7 signals were found for the tmp ring of 5.1, while 9 different signals are found in 5.2 (see Fig. 5.3). The reason for this is simply the inequivalence of the methyl groups bound to identical carbon atoms (C2 or C6). One of the methyl groups is situated *cis* to the Cp-ring, one is *cis* to the CO ligand, resulting in their non-equivalence. Otherwise, the tmp region is similar to that found in 5.1. The quaternary carbons are found at $\delta^{13}\text{C} = 56.8$ and 59.9 ppm, and are thus shifted downfield from those in the free ligand by 0.2 and 3.3 ppm, respectively. C3 and C5 are similarly shifted by 1.1 and 1.7 ppm, respectively, to lower field. Thus, as in 5.1, more electron density is drawn out of the tmp ring in the coordinated than in the non-coordinated $\text{B}=\text{C}$ unit.

The fluorene region of the ^{13}C -NMR spectrum confirms the lack of symmetry relative to the fluorenyl ligand: 12 signals are found for the two six-membered rings. C10 and C10' are shifted further downfield relative to $\text{tmpB}=\text{CR}_2$ than in 5.1 ($\delta^{13}\text{C} = 155.9$ and 157.4 ppm), whereas C15 and C15' ($\delta^{13}\text{C} = 137.6$ and 138.0 ppm) are slightly upfield from C15 in 5.1 ($\delta^{13}\text{C} = 138.4$ ppm). The remaining C-atoms are all found downfield from the ligand $\text{tmpB}=\text{CR}_2$. However, as in 5.1, the magnitude of this downfield shift decreases with increasing distance from C9 (C14, 14': $\delta^{13}\text{C} = 120.5$ ppm, 120.7 ppm; in $\text{tmpB}=\text{CR}_2$, $\delta^{13}\text{C}(\text{C14}) = 119.8$ ppm).

The boron-bound carbon atom C9 is found at $\delta^{13}\text{C} = 21.7$ ppm, and is thereby shifted from the sp^2 - into the sp^3 -hybridized range of the ^{13}C -NMR spectrum.

The carbonyl ligand is found at $\delta^{13}\text{C} = 205.1$ ppm.

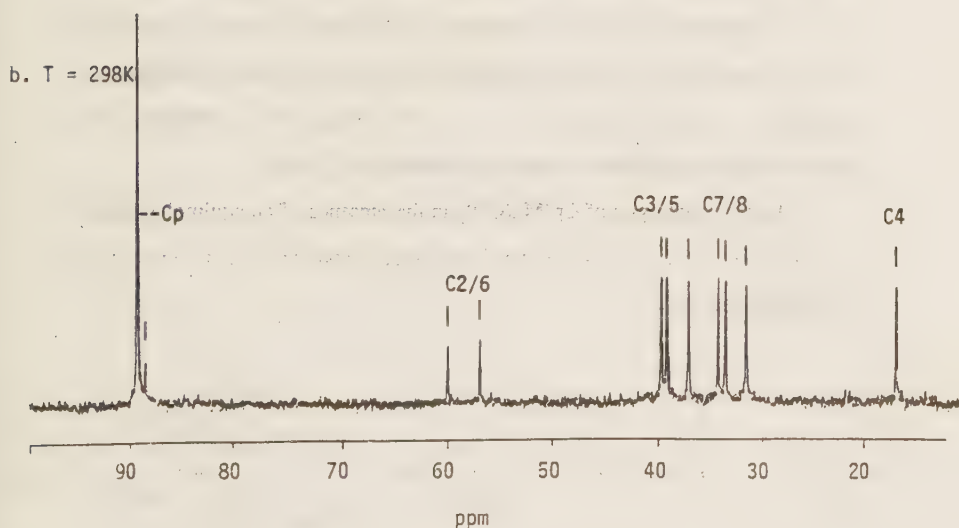
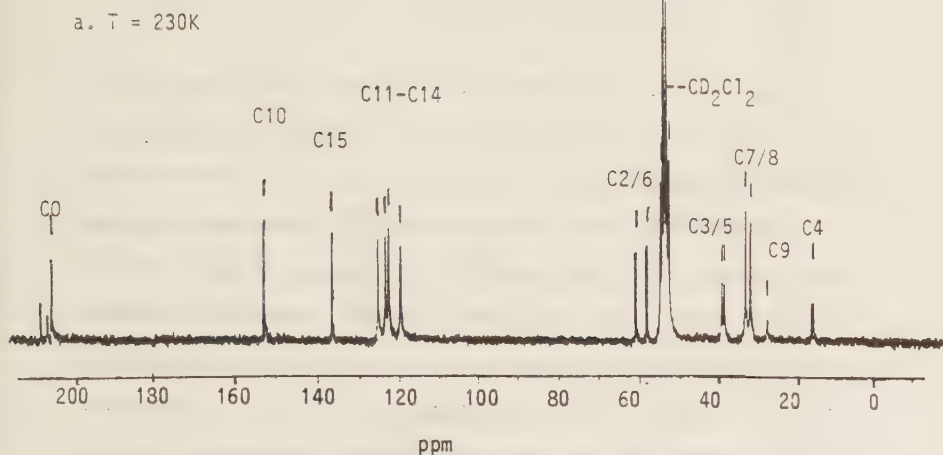


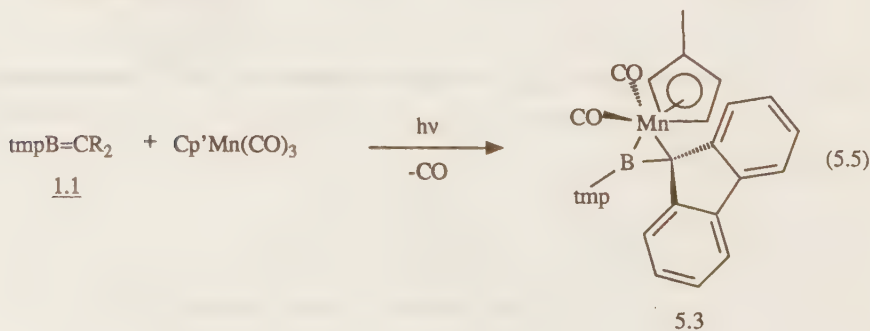
Fig. 5.3: a. ^{13}C -NMR Spectrum of 5.1

b. tmp Region of ^{13}C -NMR Spectrum of 5.2

5.4 Reaction of MeCpMn(CO)_3 with tmpB=CR_2

(Cyclopentadienyl)manganese tricarbonyl complexes are among the most inert transition metal carbonyl species known³¹. Neither CpMn(CO)_3 nor MeCpMn(CO)_3 (hereafter, MeCp will be referred to as Cp') undergoes exchange with ^{14}CO at 32°C in toluene over several weeks³². Furthermore, no reaction occurs between PPh_3 and CpMn(CO)_3 in refluxing decalin (140°C)³³. Substitution reactions have been found to proceed, however, *via* photolytic activation, and this method has been used to prepare a large number of substituted derivatives of both $\text{Cp}'\text{Mn(CO)}_3$ and CpMn(CO)_3 ³⁴. Of these monosubstituted derivatives, several have been characterized by X-ray crystallography, including the olefin complexes: $\text{CpMn(CO)}_2\text{L}$, $\text{L} = \text{CH}_2=\text{CHCOMe}$ ³⁵, $\text{Ph}_2\text{C}=\text{C}=\text{O}$ ^{24d}, and C_8H_8 ³⁶. Because of the ready availability of $\text{Cp}'\text{Mn(CO)}_3$ and the ease with which it is purified and handled, the photolytic reaction between $\text{Cp}'\text{Mn(CO)}_3$ and tmpB=CR_2 was carried out in the hope of obtaining the $\text{Cp}'\text{Mn(CO)}_2(\text{bora-alkylidene})$ complex, in analogy to 5.1 and 5.2.

Indeed, photolysis of $\text{Cp}'\text{Mn(CO)}_3$ in the presence of an equimolar amount of tmpB=CR_2 leads to the expected bora-olefin complex 5.3 in high yield, according to eq. 5.5.



5.3 is a yellow, microcrystalline solid. It is quite stable to air and fails to react with acetone at room temperature. However, the tmpB=CR_2 ligand can be

readily replaced by CO. If the reaction mixture is not flushed with N₂ gas before turning off the lamp, CO is rapidly taken up and the reaction is reversed.

5.4.1 Spectroscopic Data

The spectroscopic data for 5.3 are listed in Tables 26-29, above.

The ¹¹B-NMR spectrum contains one signal at $\delta^{11}\text{B} = 58.0$ ppm ($h_{1/2} = 560$ Hz); this represents almost no change relative to the starting material tmpB=CR₂. Only the half-width is significantly decreased.

The I.R. spectrum indicates the presence of a dicarbonyl unit with two strong absorptions found at $\nu = 1937$ and 1876 cm⁻¹. This is in contrast to the starting material Cp'Mn(CO)₃³⁶, for which two bands are found, one at 2010 cm⁻¹ and a broad band at 1910 cm⁻¹. This decrease in frequency of the CO-vibrations proves the poorer π -acceptor ability of the tmpB=CR₂ ligand, as compared to a CO-ligand. Otherwise, the I.R. spectrum is free of absorptions between 1498 and 1876 cm⁻¹, thereby ruling out the presence of non-coordinated tmpB=CR₂.

The ¹H-NMR spectrum, because of signal broadening caused by paramagnetic impurities, proved difficult to interpret: The tmp region of 5.3 extends over a large range compared to the starting material ($\delta^1\text{H} = 0.61$ - 2.01 ppm). The four Cp' protons are split into two groups of 2H at $\delta^1\text{H} = 3.63$ and 3.90 ppm. Though this inequivalence could be explained by the asymmetry of the Cp' ring caused by the presence of the methyl group, the magnitude of this difference in 5.3 ($\Delta\delta = 0.27$ ppm) is large when one considers that these protons are found to be equivalent in the starting material Cp'Mn(CO)₃³⁷. As could later be confirmed by a crystal structure (see below, section 5.4.2), two of the four protons are directly above the fluorenyl ring and undergo an anisotropic high-field shift ($\delta^1\text{H} = 3.63$ ppm), whereas the remaining two are situated away from the fluorene ring system and are found in the expected region. The large difference in chemical shifts results not from the asymmetric position of the protons relative to the methyl

group, but from their different positions relative to the fluorenyl ligand.

The ^{13}C -NMR spectrum of 5.3 is in consonance with the suggested structure. In the tmp region, only six signals are found, presumably because of the coincidental magnetic equivalence of C7 and C8. This is supported by the much greater intensity (*ca.* 4:1) of this signal relative to the other tmp signals. The two signals for C2 and C6 at $\delta^{13}\text{C} = 59.0$ and 63.3 ppm represent large downfield shifts relative to the starting ligand tmpB=CR₂ ($\Delta = 2.7$ ppm and 7.1 ppm, respectively); the signal at 63.3 ppm is the furthest downfield yet encountered in the series 5.1 - 5.3.

The Cp' carbon atoms are found at three different locations: $\delta^{13}\text{C} = 89.8$, 90.9, and 101.9 ppm. The latter signal is for the methyl-bound C-atom and is nearly identical to that found in the starting material ($\delta^{13}\text{C} = 102.8$ ppm). The other two signals, however, are significantly downfield from the starting material, for which $\delta^{13}\text{C} = 82.3$ ppm. That two signals are found instead of one is consistent with the ^1H -NMR spectrum discussed above.

Like 5.1, but in contrast to 5.2, 5.3 possesses a plane of symmetry perpendicular to the fluorene ring system, as evidenced by the NMR data and, therefore, only six signals are found in the aromatic region. As in 5.1 and 5.2, these signals are shifted to extremely low field relative to the starting material tmpB=CR₂. The ^{13}C -NMR signal for C10 at 158.4 ppm is 14.3 ppm downfield from C10 in the uncoordinated ligand and even more deshielded than in 5.1 or 5.2. The two CO ligands are represented by a single signal at $\delta^{13}\text{C} = 230.5$ ppm.

The boron- and manganese-bound carbon atom, C9, is found at $\delta^{13}\text{C} = 24.2$ ppm, in the aliphatic region of the spectrum.

5.4.2 X-ray Crystal Structure of 5.3

An ORTEP plot of the molecule is depicted in Fig. 5.4 and selected bond lengths and angles are listed in Tables 32 and 33, respectively.

The B-C bond distance (1.518(5) Å) is identical to that found in 5.1 (1.518(7) Å). However, whereas the Fe-C distance in 5.1 was found to be longer than the Fe-B distance by *ca.* 0.6 Å, in 5.3 M-B and M-C bond lengths are much closer with the Mn-B bond being slightly (0.01 Å) longer than the Mn-C bond. However, the average distance ((M-B)+(M-C))/2 of 2.15 Å is nearly identical to that found for 5.1 (2.16 Å). The B-N bond length of 1.396(5) Å is longer than that found in either the free ligand (1.353(3) Å) or 5.1 (1.377(6) Å), but its B-N double-bond character nonetheless remains.

The angle at Mn, C1-Mn-B = 41.2(1)° is identical to the corresponding angle at the Fe center in 5.1 (C1-Fe-B = 41.2(2)°). The angle Mn-B-C1 = 68.9(2)° is slightly smaller than the corresponding Fe-B-C1 angle (71.7(2)°). The Mn-B-N angle (151.1(3)°) is slightly larger than that found in 5.1: Fe-B-N = 146.0(3)°.

The geometry at the Mn-center is pseudo-tetrahedral as evidenced by the angle formed by the two carbonyl groups at manganese: C29-Mn-C30 = 103.4(2)°. The carbonyls are furthermore slightly bent with respect to manganese from the ideal 180° angles: O-C29-Mn = 171.7(4)° and O-C30-Mn = 170.7(4)°.

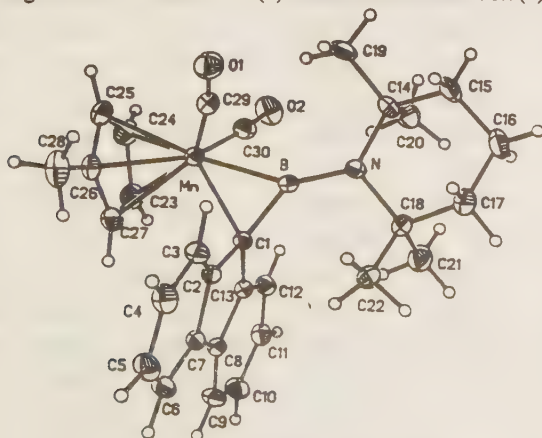


Fig. 5.4: ORTEP Plot of the compound 5.3

Table 32: Selected Bond Lengths (in Å) in 5.3. The atoms are numbered as in the ORTEP Plot (Fig. 5.4)

Mn	-C(1)	2.148(4)	Mn	-B	2.162(5)
Mn	-C(23)	2.155(5)	Mn	-C(24)	2.140(6)
Mn	-C(25)	2.150(6)	Mn	-C(26)	2.199(4)
Mn	-C(27)	2.181(4)	Mn	-C(29)	1.773(5)
Mn	-C(30)	1.762(4)	C(1)	-C(2)	1.485(4)
C(1)	-C(13)	1.482(5)	C(1)	-B	1.518(5)
C(2)	-C(7)	1.417(5)	C(8)	-C(13)	1.413(4)
C(8)	-C(9)	1.398(6)	C(9)	-C(10)	1.375(6)
C(10)	-C(11)	1.386(5)	C(11)	-C(12)	1.389(6)
C(12)	-C(13)	1.390(5)	B	-N	1.396(5)
N	-C(14)	1.543(4)	N	-C(18)	1.555(6)
C(14)	-C(15)	1.540(6)	C(15)	-C(16)	1.503(8)
C(16)	-C(17)	1.510(5)	C(14)	-C(20)	1.539(6)
C(29)	-O(1)	1.163(6)	C(30)	-O(2)	1.170(5)

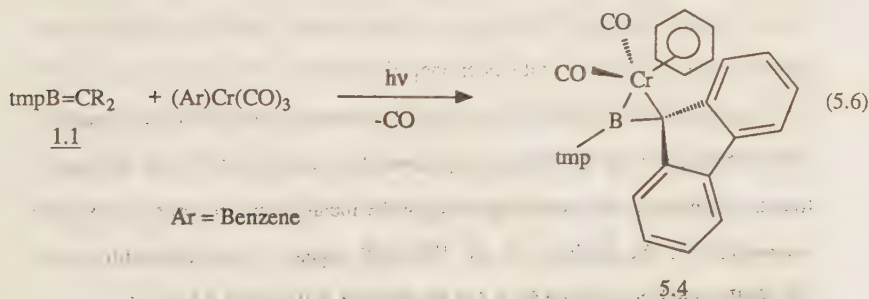
Table 33: Selected Bond Angles (in degrees) in 5.3. The atoms are numbered as in the ORTEP Plot (Fig. 5.4)

C(1)	-Mn	-B	41.2(1)	B	-Mn	-C(23)	132.6(2)
B	-Mn	-C(24)	156.7(2)	C(1)	-Mn	-C(23)	100.1(2)
C(1)	-Mn	-C(24)	138.6(2)	C(23)	-Mn	-C(24)	38.6(2)
B	-Mn	-C(29)	76.9(2)	B	-Mn	-C(30)	76.0(2)
C(23)	-Mn	-C(29)	149.2(2)	C(23)	-Mn	-C(30)	94.1(2)
C(24)	-Mn	-C(29)	118.2(2)	C(24)	-Mn	-C(30)	82.9(2)
Mn	-C(1)	-C(2)	113.0(3)	Mn	-C(1)	-C(13)	114.0(3)
Mn	-C(1)	-B	69.9(2)	C(2)	-C(1)	-B	126.3(3)
Mn	-B	-C(1)	68.9(2)	Mn	-B	-N	151.1(3)
C(1)	-B	-N	140.0(4)	B	-N	-C(14)	125.1(3)
B	-N	-C(18)	117.8(3)	C(14)	-N	-C(18)	115.8(3)
N	-C(14)	-C(19)	111.1(3)	Mn	-C(23)	-C(24)	70.1(3)
Mn	-C(23)	-C(27)	72.2(3)	Mn	-C(26)	-C(28)	129.5(4)
Mn	-C(29)	-O(1)	171.7(4)	Mn	-C(30)	-O(2)	170.7(4)

5.5 Reaction of $(\eta^6\text{-Benzene})\text{Cr}(\text{CO})_3$ with $\text{tmpB}=\text{CR}_2$

Like $\text{CpMn}(\text{CO})_3$, $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ undergoes photolytic substitution reactions to yield $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_2(\text{mono-olefin})$ complexes ³⁸⁻⁴¹. They tend, however, to be much less stable than their $\text{CpMn}(\text{CO})_2$ analogues and have only been characterized by analysis and I.R. However, because of the now-known stabilizing ability of the $\text{tmpB}=\text{CR}_2$ ligand, it was hoped that reaction between $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ and $\text{tmpB}=\text{CR}_2$ would yield a stable bora-olefin complex.

Photolysis of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in the presence of an equimolar amount of $\text{tmpB}=\text{CR}_2$ resulted in formation of 5.4 according to eq. 5.6.



The product 5.4 is a light orange solid only slightly soluble in toluene. It could be fully characterized. Spectroscopic data for 5.4 are listed, along with those of 5.1-5.3, in Tables 26-29 (see above).

5.5.1 Spectroscopic Data

The infrared spectrum contains two sharp carbonyl absorptions at $\nu = 1889$ and 1841 cm^{-1} . Both are at lower frequency as compared with $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ ($\nu = 1987, 1817\text{ cm}^{-1}$) in accord with the relatively weak π -acceptor property of the $\text{tmpB}=\text{CR}_2$ ligand ⁴². $\nu(\text{N}=\text{B}=\text{C})$ at 1717 cm^{-1} is no longer present. The carbonyl

regions of the I.R. spectra of 5.2-5.4 are presented in Fig. 5.5.

NMR characterization of 5.4 is complicated by its poor solubility in organic solvents and its tendency to decompose fairly rapidly in solution unless stored at below -20°C . In the solid state, on the other hand, 5.4 is remarkably stable and seems unaffected by both water and air. In CDCl_3 , it decomposes within 5 minutes. However, in C_6D_6 , good spectra (^1H , ^{11}B , ^{13}C) were obtained as long as the samples were concentrated and the pulse times short (pulsing overnight only led to the presence of increasing amounts of impurities).

The ^{11}B -NMR spectrum of 5.4 indicates the completion of an emerging pattern from 5.1 through 5.4. Though the signals are all fairly close to that found for uncomplexed $\text{tmpB}=\text{CR}_2$ ($\delta^{11}\text{B} = 59.2 \text{ ppm}^{21}$), a series emerges from Cr to Co, wherein slight downfield shifts occur as one moves from left to right in the periodic table. This agrees with electronegativity trends. Thus, between 5.4 ($\delta^{11}\text{B} = 57.2 \text{ ppm}$) and the $\text{CpCo}(\text{CO})$ complex 5.2 (representing the most electropositive and electronegative of the metals, respectively), a value for $\Delta\delta^{11}\text{B}$ of 4.0 ppm is found. In this way, the electronegativity of the metal bound to boron seems to be responsible for the position of the ^{11}B -NMR signal. The half-width of the ^{11}B -NMR signal ($h_{1/2} = 500$) for 5.4 is the smallest in the series 5.1 to 5.4.

Because of the poor solubility and, as mentioned, the presence of decomposition products in solution, the ^1H -NMR spectrum of 5.4 cannot be easily interpreted. The tmp region is rather broad ($\delta^1\text{H} = 0.75 \text{ ppm} - 2.16 \text{ ppm}$) and, thus, hindered rotation about the B-N bond can be inferred, as is found in the complexes 5.1-5.3. The protons of the arene ligand attached to Cr are divided into two sets of 3H at $\delta^1\text{H} = 3.81$ and 3.99 ppm , implying a lack of symmetry and hindered rotation, similar to that found in the MeCp-ligand of 5.3.

The ^{13}C -NMR spectrum is similar to those obtained for 5.1-5.3. 7 tmp signals are found, all shifted downfield relative to the uncoordinated ligand. The C2,6 signals at $\delta^{13}\text{C} = 59.7$ and 63.3 ppm are very similar to those found for 5.3 ($\delta^{13}\text{C} = 59.0, 63.3 \text{ ppm}$), as are those found for C3,5 at $\delta^{13}\text{C} = 38.6$ and 39.7 ppm (in 5.3, $\delta^{13}\text{C} = 38.6$ and 39.5 ppm).

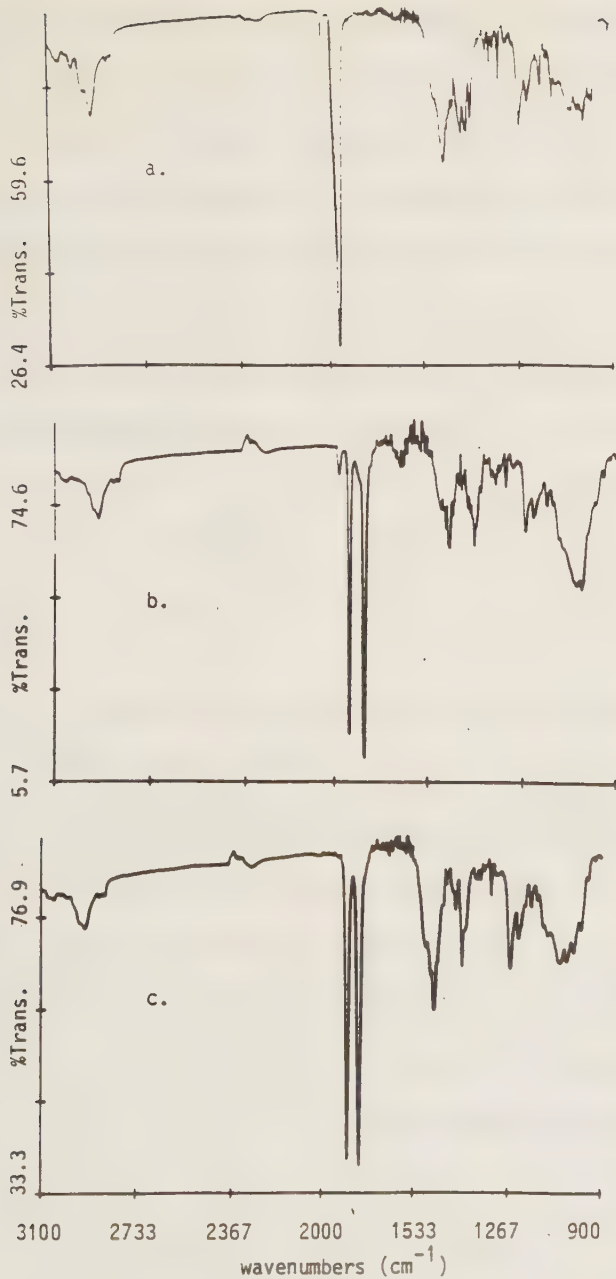


Fig. 5.5: I.R. Spectra of the compounds:

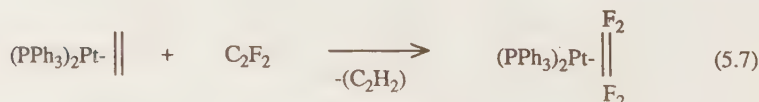
a. 5.2, b. 5.3, c. 5.4

In accord with the ^1H -NMR spectrum, in which the arene protons were found to be non-equivalent, three different ^{13}C -NMR signals are observed at $\delta^{13}\text{C} = 97.8, 100.0$ and 104.3 ppm, all of relatively equal intensity, thus implying the presence of a plane of symmetry which bisects two C-C bonds in the benzene ring. This is borne out by the presence of only four ^{13}C -NMR signals for the H-bound C-atoms in the two six-membered fluorenyl rings. The symmetry with respect to fluorene is, however, not perfect, as evidenced by the presence of four signals for C10, C10', C15 and C15'. The differences between the signal positions of $\Delta\delta^{13}\text{C} = 0.1$ ppm for C 15/15' and $\Delta\delta^{13}\text{C} = 0.2$ ppm for C 10/10' are not large, however, thus implying only a slight distortion from a symmetrical arrangement. Likewise, the carbonyl signals are found as a pair at $\delta^{13}\text{C} = 187.6$ ppm and 188.2 ppm.

The B- and Cr-bound C-atom, C9, is found at $\delta^{13}\text{C} = 26.2$ ppm. Spectroscopic data for 5.4 can be found in Tables 26-29.

5.6 Reaction of $\text{tmpB}=\text{CR}_2$ with Transition Metal-Olefin Complexes

Transition metal-olefin complexes which contain labile or volatile olefin species are often used as starting materials in ligand-substitution reactions. Examples of such reactions using various metals and either ethylene, cyclooctadiene (COD), or isopropene are abundant in the literature¹⁹⁾. Of particular interest for the present work was the reaction between tetrafluoroethylene and bis(triphenylphosphine)Pt(ethylene) to yield the tetrafluoroethylene complex (eq. 5.7)⁴³⁾.

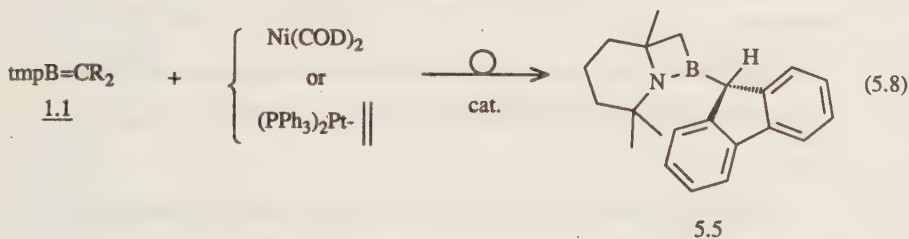


Reacting equimolar amounts of $\text{tmpB}=\text{CR}_2$ and $(\text{PPh}_3)_2\text{Pt}(\text{ethylene})$ in

toluene at room temperature resulted in no evolution of C_2H_4 . However, after a reaction time of 12h, ^{11}B -NMR indicated the presence of a new compound at $\delta^{11}B = 43.5$ ppm ($h_{1/2} = 230$ Hz), which could not be isolated in a pure state.

Similarly, reaction of $tmpB=CR_2$ with $Ni(COD)_2$ in toluene at room temperature led to a single product at $\delta^{11}B = 43.3$ ppm ($h_{1/2} = 280$ Hz), the identity of which could not be determined because it could not be cleanly isolated.

For lack of other data, and because of the large number of transition metal complexes known to catalyse a rearrangement of $tmpB=CR_2$ (see above, section 3.4 and Ref. 47), it was concluded that these two species also catalytically rearrange $tmpB=CR_2$ to the product 5.5 (eq.5.8).



The mechanism of this rearrangement is not known, but the nature of the product 5.5 has been thoroughly investigated (C-, H-, N-analysis; ^{11}B -, 1H -, ^{13}C -NMR; mass spectroscopy)⁴⁴.

Experimental Section

General Procedures and Methods

Because of the extreme air- and moisture-sensitivity of most of the compounds used in this work, the reactions--unless otherwise indicated--were carried under an atmosphere of dry nitrogen or argon. The apparatus (Schlenk-apparatus, NMR tubes) were evacuated and dried with a heat gun or an open flame.

All solvents were dried, distilled, and degassed according to standard laboratory procedures¹⁾ and stored under inert atmosphere (nitrogen, argon) prior to use.

For nuclear magnetic resonance spectroscopy, the following systems were used: Varian FT 80 (¹¹B, ³¹P), Jeol FX 90Q (¹H, ¹¹B, ¹³C, ¹⁹F, ¹¹⁹Sn) and Bruker WP 200 and AC 200 (¹¹B, ¹³C, ¹⁴N, ¹¹⁹Sn). The following NMR standards were used: internal TMS (¹H, ¹³C), internal CDCl₃ ($\delta^{13}\text{C} = 77.0$, $\delta^1\text{H} = 7.24$), internal CD₂Cl₂ ($\delta^{13}\text{C} = 53.8$, $\delta^1\text{H} = 5.33$), internal C₆D₆ ($\delta^{13}\text{C} = 128.0$, $\delta^1\text{H} = 7.15$), internal d⁸-toluene ($\delta^{13}\text{C} = 20.4$, $\delta^1\text{H} = 2.09$)--the obtained values were recalculated relative to TMS--, external BF₃·OEt₂ (¹¹B), external saturated aq. solution of NaNO₃ (¹⁴N), external CFCl₃ (¹⁹F), 85% aq. solution of H₃PO₄ (³¹P) and external SnMe₄ (¹¹⁹Sn).

Chemical shifts are given in ppm. A downfield shift (shift to higher frequency) relative to standard is indicated by a positive sign.

Infrared spectra were recorded (in Nujol/Hostaflon or the indicated solvent) on a Perkin-Elmer 325 or on a Varian FT-I.R. spectrometer.

Mass spectra were recorded on an Atlas CH7-spectrometer. Solids were transferred from a glass tube directly to the ion source. For the calculation of isotope patterns, an Olivetti P 6060 system, equipped with a program developed by

Dr. F. Bachmann, was used.

Melting points were determined in sealed capillary tubes under inert atmosphere and are uncorrected.

C-, H-, N- and S-analyses were carried out in the Microanalytical Laboratories of the Institute for Inorganic Chemistry of the University of Munich. Differences between calculated and found values in the case of highly sensitive substances result from insufficient precautionary procedures when weighing or from the formation of boron carbide in the case of organoboranes (C-values too low). Halide analyses were carried out by means of an automatic titrator (Titrigraph) following hydrolysis.

The NMR and I.R. data of the prepared compounds are found either in the Experimental Section with the corresponding Experiment or in the indicated Tables.

Starting Materials

Purchased materials:

In addition to substances purchased in the Chemical Stores of the Inorganic and Organic Institutes, the following chemicals were purchased from common sources:

BCl_3 ; 2,2,6,6-tetramethylpiperidine; $^n\text{BuLi}$; MeLi ; 9H-fluorene; NaNH_2 ; TMS; C_6D_6 ; CDCl_3 ; CD_2Cl_2 ; d^8 -toluene; GeCl_4 ; SnCl_4 ; TiCl_4 ; TiBr_4 ; $\text{Ti}(\text{O}^i\text{Pr})_4$; HfCl_4 ; PCl_3 ; PBr_3 ; AsCl_3 ; $\text{P}(\text{OMe})_3$; BiCl_3 ; $[\text{CpFe}(\text{CO})_2]_2$; CH_3COCl ; PPh_2Cl ; PPhCl_2 ; 2-hydroxy-phenol; $\text{Fe}(\text{CO})_5$; $(\text{MeCp})\text{Mn}(\text{CO})_3$; $\text{CpCo}(\text{CO})_2$ (as a soln. in cyclopentadiene); $\text{Ni}(\text{COD})_2$; $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$.

Compounds used in this work which were received as donations (to the

donors: 1000 Dank!);

SbCl₃, SbBr₃, AsBr₃, 2-fluoro-1,3,2-benzodioxaphospholane, 2-methoxy-1,3,2-dioxaphospholane, 2-chloro-1,3,2-benzodioxaphospholane, 2-chloro-1,3,2-benzodioxastibolane (A. Brandl); 2-fluoro-1,3,2-benzodioxastibolane (Inorganic Laboratory Course III); P(NMe₂)₃ (P. Mayer); Ti(NMe₂)Cl₃ (B. Stöber); BzPCl₂ (G. Linti, M. Wagner); Me₂SnCl₂, Me₂SnBr₂, Me₃SnCl (W. Storch, M. Kaufmann); N,N-dimethylglycine (G. Geisberger); Fe₂(CO)₉ (W. Rattay); Re(CO)₅BF₄ (P. Fritz, E. Fritsch); Fp₂CS₂ (P. Fritz); (PPh₃)₂Pt(C₂H₂), Ni(COD)₂ (J. Müller).

The following compounds were prepared according to literature procedures:

tmpBCl₂²⁾; Li(C₁₃H₉), tmpBCl(C₁₃H₉), tmpBCl(C₁₃H₈)³⁾; NaN(SiMe₃)₂⁴⁾; Cp₂Ti(CH₃)₂⁵⁾; CpFe(CO)₂COCH₃⁶⁾; CpRu(PPh₃)₂C≡CPh⁷⁾; CpRu(PPh₃)₂Cl⁸⁾; 2-chloro-1,3,2-benzodioxaphospholane⁹⁾; 2-bromo-1,3,2-benzodioxaphospholane¹⁰⁾; 2-chloro-1,3,2-dioxaphospholane¹¹⁾; ClP(OMe)₂¹²⁾; Cl₂P(NMe₂), ClP(NMe₂)₂¹³⁾.

Experiments to Chapter 1

Experiment 1.1: Chloro[9-(dichlorophosphino)fluorenyl](2,2,6,6-tetramethyl-piperidino)borane

To 2.00 g (6.3 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added with stirring 0.87 g (6.3 mmol) PCl_3 in 15 ml toluene over 10 min. The solution became noticeably lighter in color upon addition. ^{11}B -NMR indicated the presence of one new product at $\delta^{11}\text{B} = 43.0$ ppm. All volatiles were removed *in vacuo* and the resulting brown to colorless oily solid dissolved in warm hexane:toluene (*ca.* 2:1) and the solution filtered. The filtrate was cooled to -20°C for 12h followed by 2h at -78°C whereby large, pink-tinted prisms formed. The product was separated by filtration, washed with pentane (2 x 5 ml) and dried *in vacuo* to yield 1.74 g 1.2 (60%), m.p. = $164\text{--}166^\circ\text{C}$.

$\text{C}_{22}\text{H}_{26}\text{BCl}_3\text{NP}$ (452.60)

calc.	C 58.38	H 5.79	N 3.09
found	C 58.81	H 6.19	N 3.20

Mol. wt. (MS): 451 (^{11}B , ^{35}Cl)

Spectroscopic Data: Tables 1-3

Experiment 1.2: Bromo[9-(dibromophosphino)fluorenyl](2,2,6,6-tetramethyl-piperidino)borane, 1.3

To 2.17 g (6.8 mmol) $\text{tmpB}=\text{CR}_2$ in 35 ml toluene was added with stirring 1.84 g (6.8 mmol) PBr_3 in 5 ml toluene over 10 min. The solution took on a much lighter color and the flask became slightly warm. The reaction mixture was stirred for 12h at 25°C , at which time a ^{11}B -NMR spectrum indicated the presence of a single product ($\delta^{11}\text{B} = 43.0$ ppm). All volatiles were removed *in vacuo* and the

resulting colorless solid was taken up in hexane:toluene (2:1, 20 ml) and filtered. Cooling the filtrate to -20°C for 12h and -78°C for 3h yielded a colorless crystalline solid which was separated by filtration, washed with pentane (2 x 10 ml), and dried *in vacuo*. Yield: 1.79 g 1.3 (45%), m.p. = 128-131°C.

$C_{22}H_{26}BBr_3NP$ (585.97)

calc.	C 45.10	H 4.47	N 2.39
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found	C 44.60	H 4.99	N 2.38
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Mol. wt. (MS): 394 (^{11}B , ^{79}Br , M-PBr₂)

Spectroscopic Data: Tables 1-3

Experiment 1.3a: Reaction of tmpB=CR₂ with tris(dimethylamino)phosphane

To 1.15 g (3.7 mmol) tmpB=CR₂ in 20 ml toluene was added with stirring a solution of P(NMe₂)₃ (0.80 g, 4.9 mmol) in 25 ml toluene. No apparent reaction was observed (no color change, no warming of the flask). The mixture was stirred for 12h, after which a ^{11}B -NMR spectrum indicated the presence of unreacted tmpB=CR₂ ($\delta^{11}B$ = 58.3 ppm, $h_{1/2}$ = 760 Hz) and a ^{31}P -NMR spectrum no other product than P(NMe₂)₃ ($\delta^{31}P$ = 123 ppm). After stirring at room temperature for 27d, no further changes had occurred.

Experiment 1.3b: Reaction of tmpB=CR₂ with tris(methoxy)phosphane

To 1.20 g (3.8 mmol) tmpB=CR₂ in 20 ml toluene was added with stirring an excess of P(OMe)₃ dissolved in 20 ml toluene. No apparent reaction occurred. The ^{11}B -NMR spectrum after 12h indicated the presence of starting material ($\delta^{11}B$ = 59.1 ppm, $h_{1/2}$ = 730 Hz) and the ^{31}P -NMR spectrum also showed no reaction. No change in the spectra occurred after 12d.

Experiment 1.4: Reaction of $\text{tmpB}=\text{CR}_2$ with (dimethoxy)chlorophosphane

To 1.20 g (3.8 mmol) $\text{tmpB}=\text{CR}_2$ in 20 ml toluene was added with stirring a slight excess of slightly impure (by ^{31}P -NMR) $(\text{OMe})_2\text{PCl}$ (0.60 g, 4.7 mmol) in 10 ml toluene over 10 min. The solution became lighter in color, but no noticeable warming was observed. After stirring for 3h at RT, the ^{11}B -NMR spectrum indicated complete reaction to one new product at $\delta^{11}\text{B} = 27.9$ ppm ($h_{1/2} = 90$ Hz). The ^{31}P -NMR spectrum contained 4 signals at 216, 191, 170, and 142 ppm. The latter two signals were also found in the starting material: 170 ppm for $(\text{OMe})_2\text{PCl}$ and 142 ppm for $\text{P}(\text{OMe})_3^*$. Using the relative intensities of the $\text{P}(\text{OMe})_3$ and $(\text{OMe})_2\text{PCl}$ signals as a guide (10:1 in the starting material *versus* 1:1 in the reaction mixture), it appeared that 90% of the $(\text{OMe})_2\text{PCl}$ reacted (90% roughly corresponds to 4.0 mmol). Attempts to isolate any of the products from solvent mixtures (toluene, hexane, pentane) at lower temperatures failed.

* The synthesis of $(\text{OMe})_2\text{PCl}$ requires an excess of $\text{P}(\text{OMe})_3$ which cannot be separated.

Experiment 1.5: Reaction of $\text{tmpB}=\text{CR}_2$ with bis(dimethylamino)chlorophosphane

To 1.55 g (4.9 mmol) $\text{tmpB}=\text{CR}_2$ was added with stirring a solution of freshly prepared $(\text{Me}_2\text{N})_2\text{PCl}$ (0.76 g, 4.9 mmol) in 20 ml toluene. The solution became lighter in color and the flask slightly warm. After stirring for 2h at RT, the ^{11}B -NMR spectrum indicated the presence of starting material ($\delta^{11}\text{B} = 59.5$ ppm) and a new product ($\delta^{11}\text{B} = 31.6$ ppm, $h_{1/2} = 80$ Hz) ($I = 1:1$). Addition of a second equivalent of $(\text{Me}_2\text{N})_2\text{PCl}$ resulted in the complete disappearance of the starting material, leaving the single sharp signal at $\delta^{11}\text{B} = 31.6$ ppm. All attempts to isolate a solid product from hexane, pentane and toluene mixtures at lower temperature failed.

Experiment 1.6: Chloro[9-(chloro(dimethylamino)phosphino)fluorenyl]-(2,2,6,6-tetramethylpiperidino)borane, 1.6

To 1.41 g (4.5 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added with stirring a solution of 0.66 g (4.5 mmol) $(\text{Me}_2\text{N})\text{PCl}_2$ in 15 ml hexane:toluene (2:1) over 10 min. The solution turned lighter in color and the flask became slightly warm. After 2h, a ^{11}B -NMR spectrum indicated complete reaction to 1.6. All volatiles were removed *in vacuo* to yield a dark brown oil which was taken up in 5 ml toluene. 20 ml hexane was added and the solution was warmed to 40°C (water bath) until all solid material had dissolved. Cooling to -20°C for 12h and to -78°C for 2h yielded 1.25 g 1.6 (60%) as a colorless crystalline solid, m.p. = 96°C (dec.).

$\text{C}_{24}\text{H}_{32}\text{BCl}_2\text{N}_2\text{P}$ (461.23)

calc.	C 62.50	H 6.99	N 6.07
found	C 63.35	H 7.45	N 9.27

Spectroscopic Data: Tables 1-3

Experiment 1.7: Reaction of tmpPCl_2 with $\text{tmpB}=\text{CR}_2$

To 1.48 g (4.7 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added with stirring a solution of 1.14 g (4.7 mmol) tmpPCl_2 in 15 ml toluene over 10 min. No apparent reaction occurred. The solution was stirred at RT for 24h, after which time a ^{11}B -NMR spectrum indicated only unreacted educt. After a further 4d the spectrum had remained unchanged ($\delta^{11}\text{B} = 59.0$ ppm, $h_{1/2} = 610$ Hz). A ^{31}P -NMR spectrum indicated only the presence of tmpPCl_2 ($\delta^{31}\text{P} = 164$ ppm).

Experiment 1.8: Reaction of $\text{tmpB}=\text{CR}_2$ with $^t\text{BuPCl}_2$

To 2.15 g (6.8 mmol) $\text{tmpB}=\text{CR}_2$ in 35 ml toluene was added with stirring a solution of $^t\text{BuPCl}_2$ (1.21 g, 7.5 mmol) in 15 ml toluene over 10 min. No apparent reaction occurred. The reaction mixture was stirred for 12h, at which time a ^{11}B -NMR spectrum indicated the presence of $\text{tmpB}=\text{CR}_2$ ($\delta^{11}\text{B} = 59$ ppm). The solution was then heated to reflux for 3h, cooled to RT, and stirred for an additional 12h. The ^{11}B -NMR spectrum indicated the presence of two compounds at $\delta^{11}\text{B} = 59$ ($\text{tmpB}=\text{CR}_2$) and 36 ppm (rel. intensities: 4:1). $\delta^{31}\text{P} = 199$ ppm showed only the presence of $^t\text{BuPCl}_2$. Stirring for an additional 2 weeks resulted in no significant changes in the ^{11}B - and ^{31}P -NMR spectra.

Experiment 1.9: Chloro[9-(chloro(phenyl)phosphino)fluorenyl]-(2,2,6,6-tetramethylpiperidino)borane, 1.7

To 1.78 g (5.6 mmol) $\text{tmpB}=\text{CR}_2$ in 20 ml toluene was added with stirring a solution of 1.15 g PhPCl_2 (6.5 mmol) in 10 ml toluene. The solution was stirred at 25°C for 2h, whereby a white precipitate formed. The solution was stirred an additional 12h. After that time the ^{11}B -NMR spectrum indicated the presence of one boron-containing compound ($\delta^{11}\text{B} = 44$ ppm). The solution was filtered, and the colorless powder was washed with pentane (2 x 10 ml) and dried *in vacuo* to yield 1.80 g 1.7 (65%). The remaining solution was concentrated to 10 ml, pentane (10 ml) was added, and the solution was cooled to -20°C for 12h and to -78°C for 3h, whereby additional 1.7 was isolated (0.22 g) to increase the yield to 75%, m.p. = 165°C , dec.

$\text{C}_{28}\text{H}_{31}\text{BCl}_2\text{NP}$ (494.26)

calc.	C 68.04	H 6.32	N 2.83
found	C 68.42	H 6.46	N 2.89

Mol. wt. (MS) = 350 (M- PhPCl , ^{11}B , ^{35}Cl)

Spectroscopic Data: Tables 1-3

Experiment 1.10: Chloro[9-(chloro(benzyl)phosphino)fluorenyl]-
(2,2,6,6-tetramethylpiperidino)borane, 1.8

To 1.85 g (5.9 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added over 5 min. with vigorous stirring a solution of 1.13 g (5.9 mmol) BzPCl_2 in 15 ml toluene. The solution gradually turned darker in color, but no warming was observed. After 12h a ^{11}B -NMR spectrum indicated complete reaction to 1.8. All volatiles were removed *in vacuo* and the resulting brownish solid was taken up in a minimum of toluene (*ca.* 10 ml), and an additional 10 ml hexane was added. The resulting solution was cooled to -20°C for 12h and to -78°C for 2h to yield 1.52 g 1.8 (51%), m.p. = 145°C .

$\text{C}_{29}\text{H}_{33}\text{BCl}_2\text{NP}$ (508.28)

calc.	C 68.53	H 6.54	N 2.76
found	C 66.71	H 6.64	N 4.42

Spectroscopic Data: Tables 1-3

Experiment 1.10a: Reaction of Chloro[9-(chloro(benzyl)phosphino)fluorenyl]-
(2,2,6,6-tetramethylpiperidino)borane with $\text{NaN}(\text{SiMe}_3)_2$ to the phosphathene, 1.9

To 0.49 g (1.0 mmol) 1.8 in 30 ml toluene was added 0.18 g (1.0 mmol) $\text{NaN}(\text{SiMe}_3)_2$ as a solid, and the solution was stirred for 24h at RT. A ^{11}B -NMR spectrum indicated the presence of one boron-containing product ($\delta^{11}\text{B} = 40$ ppm) while a ^{31}P -NMR spectrum provided evidence for both the starting material ($\delta^{31}\text{P} = 138$ ppm) and a new compound ($\delta^{31}\text{P} = 289$ ppm, I = 1:1). Additional $\text{NaN}(\text{SiMe}_3)_2$ was added (0.10 g, 0.6 mmol) and the reaction mixture stirred for 24h. The ^{31}P -NMR spectrum at that time showed complete reaction to 1.9 ($\delta^{31}\text{P} = 290$ ppm, smaller peak at 289 ppm for the second isomer). Filtration, followed by

complete removal of solvent yielded a brown oil. This was dissolved in 2 ml toluene and further diluted with 10 ml hexane. The solution was cooled to -20°C and to -78°C, but no crystalline product separated out. Attempts were made at crystallization from pentane and hexane (pure) as well, but to no avail.

NMR Data (C₆D₆):

$$\delta^{11}\text{B} = 38.3 \text{ (} h_{1/2} = 580 \text{ Hz)}$$

$$\delta^{31}\text{P} = 290, 289 \text{ (rel. intensities: 3:1)}$$

Experiment 1.11: Chloro[9-(dimethylphosphino)fluorenyl](2,2,6,6-tetramethylpiperidino)borane, 1.11

To 1.46 g (4.6 mmol) $\text{tmpB}=\text{CR}_2$ in 10 ml toluene was added with stirring a solution of Me_2PCl (0.44 g, 4.6 mmol) in 15 ml toluene over 10 min. The solution turned light red in color, but did not become noticeably warm. After stirring for 2d, a ^{11}B -NMR spectrum revealed the presence of two boron-containing compounds with signals at $\delta^{11}\text{B} = 48.4$ ppm ($h_{1/2} = 330$ Hz) and 33.6 ppm ($h_{1/2} = 60$ Hz) (rel. intensities: 3:1). The ^{31}P -NMR spectrum contained two signals at $\delta^{31}\text{P} = -4$ ppm and -27 ppm ($I = 3:1$). All volatiles were removed *in vacuo* and replaced with 5 ml toluene and 20 ml hexane. Cooling to -20°C for several days yielded a yellow powder which was filtered off, washed with pentane (2 x 5 ml) and dried *in vacuo* (0.38 g). A ^{11}B -NMR spectrum in C₆D₆ indicated the presence of no boron; a ^{31}P -NMR spectrum contained one signal at $\delta^{31}\text{P} = 94$ ppm and a second broader signal ($h_{1/2} = 60$ Hz) at $\delta^{31}\text{P} = 60$ ppm. ^1H - and ^{13}C -NMR spectra could not be reasonably interpreted. All attempts to isolate a pure product were unsuccessful.

Spectroscopic Data: Table 1

Experiment 1.12: Chloro[9-(diphenylphosphino)fluorenyl](2,2,6,6-tetramethylpiperidino)borane, 1.12

To 1.82 g (5.1 mmol) $\text{tmpB}=\text{CR}_2$ in 20 ml toluene was added with stirring a solution of 1.50 g (6.8 mmol) Ph_2PCl in 15 ml toluene over 10 min. The solution became slightly lighter in color, but no warming was observed. The reaction mixture was stirred for 12h, at which time a ^{11}B -NMR spectrum indicated complete reaction to a single product ($\delta^{11}\text{B} = 45.9$ ppm). All volatiles were removed *in vacuo* at 35°C (water bath), and the resulting colorless solid dissolved in 20 ml hexane. The solution was then cooled to -20°C for 3d, whereby semi-spherical shaped platelets formed. After cooling to -78°C for an additional 3h, the solution was filtered, and the product washed with pentane (2 x 5ml) to yield 0.76 g 1.12 (36%), m.p. = $143-5^\circ\text{C}$. Attempts to increase the yield by further reduction of the solvent volume were unsuccessful.

$\text{C}_{34}\text{H}_{36}\text{BCINP}$ (535.91)

calc. C 76.20 H 6.77 N 2.61

found C 76.21 H 7.17 N 2.58

Spectroscopic Data: Tables 1-3

Experiment 1.13: Chloro[9-(chloro)fluorenyl](2,2,6,6-tetramethylpiperidino)borane, 1.13

To 2.33 g (7.4 mmol) $\text{tmpB}=\text{CR}_2$ in 35 ml toluene was added with stirring a solution of 1.55 g (7.4 mmol) PCl_5 in 15 ml CH_2Cl_2 . The reaction mixture was stirred for 12h at 25°C , whereby the solution took on a yellow color. The ^{11}B -NMR spectrum contained only a single product ($\delta^{11}\text{B} = 43.0$ ppm, $h_{1/2} = 600$ Hz), while the ^{31}P -NMR spectrum indicated the formation of PCl_3 ($\delta^{31}\text{P} = 220$ ppm). All volatiles were removed and the resulting yellow-brown oil was taken up in hexane:toluene (2:1, 20 ml) and the solution cooled to -20°C . Neither further

reduction of solvent volume nor cooling to -78°C could bring the product to crystallization.

$C_{22}H_{26}BCl_2N$ (386.20)

NMR Data:

$\delta^{11}B = 43.0$ ppm ($h_{1/2} = 600$ Hz)

Experiment 1.14: Chloro[9-(dichloroarsino)fluorenyl](2,2,6,6-tetramethylpiperidino)borane, 1.14

To 1.19 g (3.8 mmol) $tmpB=CR_2$ in 15 ml toluene was added with stirring a solution of 0.70 g (3.8 mmol) $AsCl_3$ in 5 ml toluene over 10 min. The solution became much lighter in color, and, after 2h stirring, a yellow precipitate had formed. Stirring was continued for an additional 12h, at which time only one product was observed in the ^{11}B -NMR spectrum at $\delta^{11}B = 42$ ppm. The solution was filtered and the precipitate dissolved in warm toluene:hexane (1:2), and all fractions were combined and cooled to -20°C for 12h. After cooling to -78°C for an additional 3h, large colorless crystals had formed, which were filtered off, washed with pentane (2 x 10 ml), and dried *in vacuo*. The crystals lost their form in vacuum after several hours and appeared to be light- and heat-, as well as air-sensitive. Analyses revealed the presence of 1/3 toluene molecule per molecule 1.14 (See Table 6). Yield: 1.26 g 1.14 (63%), m.p. = 137°C.

$C_{24.33}H_{28.67}AsBCl_3N$ (527.23)

calc.	C 55.43	H 5.48	N 2.62
found	C 55.11	H 5.75	N 2.90

Mol. wt. (MS): 359 (^{11}B , ^{35}Cl , M- $AsCl_2$)

Spectroscopic Data: Tables 7-9

Experiment 1.15: Bromo[9-(dibromoarsino)fluorenyl](2,2,6,6-tetramethylpiperidino)borane, 1.15

To 1.30 g (4.1 mmol) tmpB=CR_2 in 20 ml toluene was added with stirring a solution of AsBr_3 (1.29 g, 4.1 mmol) in 10 ml toluene over 10 min. After 1h the solution had turned much lighter in color, and a precipitate had formed. The ^{11}B -NMR spectrum showed the presence of a new product at $\delta^{11}\text{B} = 42$ ppm. The solution was filtered, the undissolved solid taken up in warm toluene (*ca.* 20 ml; $T = 30\text{--}35^\circ\text{C}$, compound thermally unstable!), and 10 ml hexane was added. The mixture was warmed to 35°C and stirred rapidly to insure complete dissolution. Cooling to RT resulted in the formation of large, colorless prisms. The solution was further cooled to -20°C for 12h and to -78°C for an additional 3h and filtered. The product was washed with pentane (2 x 10 ml) and dried *in vacuo*, whereby the crystals lost their form. By analysis, the product contained 1/2 molecule toluene per molecule 1.15 (see Table 6). Yield: 1.61 g 1.15 (58%), m.p. = $130\text{--}5^\circ\text{C}$, dec. The product is very light-, heat- and air-sensitive.

$\text{C}_{25.5}\text{H}_{30}\text{AsBBr}_3\text{N}$ (675.97)

calc.	C 45.31	H 4.47	N 2.07
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found	C 45.42	H 4.78	N 2.19
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Mol. wt. (MS) = 394 (^{11}B , ^{79}Br , M- AsBr_2)

Spectroscopic Data: Tables 7-9

Experiment 1.16: Reaction of tmpB=CR_2 with SbF_3

To 1.06 g (3.3 mmol) tmpB=CR_2 in 15 ml toluene was added with stirring a suspension of freshly sublimed SbF_3 (0.58 g, 3.3 mmol) in 20 ml toluene. The solution became darker in color. Over several hours, the SbF_3 dissolved completely. After stirring for 12 h, ^{11}B -NMR indicated the presence of one reaction product at $\delta^{11}\text{B} = 17.1$ ppm ($h_{1/2} = 60$ Hz). The product was suspected to

be tmpBF_2 .

Experiment 1.17: Chloro[9-(dichlorostibino)fluorenyl](2,2,6,6-tetramethyl-piperidino)borane, 1.17:

To 1.25 g (4.0 mmol) tmpB=CR_2 in 15 ml toluene was added with stirring a solution of 0.91 g (4.0 mmol) SbCl_3 in 20 ml toluene. After stirring at 25°C for 1.5 h, a colorless precipitate had formed and an ^{11}B -NMR spectrum indicated complete reaction to a new product at $\delta^{11}\text{B} = 43$ ppm. The solution was filtered, and the solid taken up in warm (35°C) hexane:toluene (1:2) and filtered and the fractions combined and cooled to -20°C for 12 h. After cooling to -78°C for an additional 3 h, the solution was filtered and the yellow-tinted prisms washed with pentane (2x10 ml) and dried *in vacuo*, whereby the crystals lost their form. The analysis indicated the presence of 1/3 molecule toluene per molecule 1.17 (see Table 6). Yield: 0.98g 1.17 (43%), m.p. = 135°C , dec.

$\text{C}_{24.33}\text{H}_{28.67}\text{BCl}_3\text{NSb}$ (574.05)

calc.	C 50.91	H 5.03	N 2.44
found	C 50.56	H 5.00	N 2.41

Mol Wt. (MS) = 350 (^{11}B , ^{35}Cl , M-SbCl₂)

Spectroscopic Data: Tables 7-9

Experiment 1.18: Bromo[9-(dibromostibino)fluorenyl](2,2,6,6-tetramethyl-piperidino)borane, 1.18

To 1.35 g (4.3 mmol) tmpB=CR_2 in 20 ml toluene was added with stirring a solution of 1.65 g (4.3 mmol) SbBr_3 in 15 ml toluene. After stirring for 1 h, the solution turned much lighter in color and a precipitate was seen to form. The solution was stirred an additional 12 h at which time the ^{11}B -NMR spectrum

indicated the presence of one new product at $\delta^{11}\text{B} = 42$ ppm. The reaction mixture was filtered and the precipitate redissolved in 20 ml warm toluene. The fractions were then combined, 10 ml hexane was added, and the solution warmed (35°C) with rapid stirring to insure complete dissolution. The mixture was cooled to -20°C for 12 h and to -78°C for an additional 3 h, whereby large prisms formed. The solution was filtered, and the product was washed with pentane (2 x 10 ml) and dried *in vacuo* to yield 1.45 g 1.18 (45%) as a toluene adduct (3 molecules toluene to 4 molecules 1.18, see Table 6), m.p. = 125°C, dec. The product lost its crystalline form in vacuum and was found to be both light- and heat-sensitive.

$\text{C}_{27.25}\text{H}_{32}\text{BBr}_3\text{NSb}$ (745.84)

calc. C 43.88 H 4.32 N 1.88

found C 44.35 H 4.38 N 2.28

Spectroscopic Data: Tables 7-9

Experiment 1.19: Chloro[9-(dichlorobismuthyl)fluorenyl](2,2,6,6-tetramethylpiperidino)borane, 1.19 :

To a stirred suspension of 1.41 g (4.5 mmol) BiCl_3 in 25 ml toluene was added a solution of 1.35 g (4.5 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene. The reaction mixture first took on an orange-yellow color and then gradually turned dark green. After stirring at room temperature for 2 days, a ^{11}B -NMR spectrum indicated that all starting material had reacted ($\delta^{11}\text{B} = 37.3$ ppm in toluene solution). As the product did not appear very soluble, the solution was filtered and the resulting solid taken up in CH_2Cl_2 . Cooling the solution to -20°C yielded an orange powder (0.34 g 1.19, (13%) m.p. = 140°C, which was filtered, washed with 2 x 5 ml pentane and dried *in vacuo*.

$\text{C}_{22}\text{H}_{26}\text{BBiCl}_3\text{N}$ (630.55)

calc.	C 41.90	H 4.16	N 2.22
found	C 39.84	H 4.03	N 2.15

Spectroscopic Data: Tables 7 and 9

Experiments to Chapter 2

Experiment 2.1: [9-(1,3,2-benzodioxaphospholano)fluorenyl](chloro)-(2,2,6,6-tetramethylpiperidono)borane, 2.1

To 2.48 g (7.9 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added with stirring a solution of 1.12 g (7.9 mmol) 2-chloro-1,3,2-benzodioxaphospholane in 15 ml toluene. The solution immediately turned lighter in color and the flask became slightly warm. The reaction mixture was stirred overnight and a ^{11}B -NMR spectrum recorded the next day indicated only one boron-containing reaction product at $\delta^{11}\text{B} = 45.6$ ppm, $h_{1/2} = 560$ Hz. Solvent was removed *in vacuo* (along with traces of the phospholane) and the resulting colorless solid taken up in a minimum amount of toluene (*ca.* 10 ml). Hexane (15 ml) was added, and the solution warmed to assist in dissolution. The solution was cooled to -20°C for 12h and -78°C for an additional 2h and a white crystalline solid was filtered off, washed with pentane (2 x 10 ml) and dried *in vacuo* to yield 2.50 g 2.1 (65%), m.p. $130^\circ - 132^\circ\text{C}$, dec.

$\text{C}_{28}\text{H}_{30}\text{BClNO}_2\text{P}$ (489.79)

calc.	C 68.66	H 6.17	N 2.86
found	C 69.13	H 6.08	N 2.83

Spectroscopic Data: Tables 10-12

Experiment 2.2: [9-(1,3,2-benzodioxaphospholano)fluorenyl](bromo)-(2,2,6,6-tetramethylpiperidino)borane, 2.2

To 2.10 g (6.7 mmol) $\text{tmpB}=\text{CR}_2$ in 20 ml toluene was added with stirring a solution of 1.46 g (6.7 mmol; slight excess can be used) of 2-bromo-1,3,2-benzodioxaphospholane in 10 ml toluene. The solution became

lighter in color upon addition of the first few drops. Addition was carried out over 10 min. and the solution then stirred overnight. All volatiles were removed *in vacuo* and the resulting solid was taken up in toluene:hexane (1:2, 30 ml) and warmed to 35°C (water bath) to aid in dissolution. The resulting solution, upon cooling to -20°C for 12 h and to -78°C for 2 h, yielded 2.18 g 2.2 (61%) as a white crystalline solid of m.p. = 124-126°C, dec. with brown decoloration.

$C_{28}H_{30}BBrNO_2P$ (534.25)

calc.	C 62.95	H 5.66	N 2.62
found	C 63.10	H 5.90	N 2.59

Spectroscopic Data: Tables 10-12

Experiment 2.3: Chloro[9-(1,3,2-dioxaphospholano)fluorenyl]-(2,2,6,6-tetramethylpiperidino)borane, 2.3

To 1.29 g (4.1 mmol) $t\text{mpB}=\text{CR}_2$ in 20 ml toluene was added with stirring a solution of 0.52 g (4.1 mmol) 2-chloro-1,3,2-dioxaphospholane in 15 ml toluene over 10 minutes. Upon addition of the first few drops, the solution became much lighter in color. After stirring at room temperature for 2 days, a ^{11}B -NMR spectrum indicated complete reaction to a new product at $\delta^{11}\text{B} = 46.4$ ppm. A ^{31}P -NMR spectrum also indicated the presence of a new product at $\delta^{31}\text{P} = 169$ ppm. All volatiles were removed *in vacuo* and the resulting brown oil taken up in 20 ml hexane, in which it dissolved completely. Upon cooling to -20°C for several days and -78°C for an additional 8h, a white powdery substance separated from the solution, which was carefully filtered, washed with pentane (2 x 2 ml) and dried *in vacuo*. Yield: 0.73 g 2.3 (41%), m.p. 101 °C, dec.

$C_{24}H_{30}BClNOP$ (425.75)

calc.	C 67.71	H 7.10	N 3.29
found	C 68.31	H 7.87	N 3.01

Spectroscopic Data: Tables 10-12

Experiment 2.4: Preparation of 2-chloro-1,3,2-tetramethylphospholane from pinacole and PCl_3

To 12.0 ml PCl_3 in 50 ml CH_2Cl_2 (18.8 g, 0.14 mol) was slowly added 16.2 g pinacole (0.14 mol) in CH_2Cl_2 : hexane (2:1, 60 ml total volume), whereby HCl(g) was given off rapidly and the reaction mixture began to reflux. The addition was made at such a rate as to keep the mixture refluxing without reacting too vigorously. After addition was complete, the mixture was allowed to cool to room temperature, whereby a white precipitate appeared. The mixture was then refluxed an additional 3h whereby the white precipitate gradually disappeared and a yellow solid formed. The reaction mixture was cooled to room temperature and the solvent was separated off from the solid *via* pipette. All volatiles were removed from the solution *in vacuo* (0°C, 5 Torr) and the resulting oil was distilled to yield a fraction of colorless liquid at b.p. = 40 - 43°C/ 5 Torr. The compound was characterized by NMR (C_6D_6).

$\delta^{31}\text{P} = 175 \text{ ppm}$

$\delta^{13}\text{C} = 24.6, 25.4 (\underline{\text{C}}\text{H}_3); 88.8 (\text{OC}\underline{\text{Me}}_2) (J = 8 \text{ Hz})$

Experiment 2.5: Chloro[9-(1,3,2-tetramethyldioxaphospholano)fluorenyl]-(2,2,6,6-tetramethylpiperidino)borane, 2.4

To 1.34 g (4.3 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added with stirring 0.80 g (4.3 mmol) 2-chloro-1,3,2-tetramethyldioxaphospholane in 15 ml toluene over 10 minutes. No change in color nor warming of the flask was detected. The solution was stirred for 24 h, at which time a ^{11}B -NMR spectrum indicated only a small amount of reaction had occurred. After 9d, 2 signals at $\delta^{11}\text{B} = 58.6$ and 46.1 ppm (rel. intensities $\cong 1:3$) were observed. The mixture was further stirred at RT. After

21d, only one boron-containing product ($\delta^{11}\text{B} = 47.6$ ppm) was present. All volatiles were then removed *in vacuo* and the resulting brown oil dissolved in 20 ml hexane. Cooling the solution to -20°C for 2d resulted in the precipitation of a white crystalline solid which was separated by filtration, washed with pentane (2 x 5 ml) and dried *in vacuo* to yield 0.99 g 2.4 (46%), m.p. = $105 - 108^\circ\text{C}$.

$\text{C}_{28}\text{H}_{38}\text{BCINO}_2\text{P}$ (497.86)

calc.	C 66.63	H 7.63	N 2.77
found	C 67.55	H 7.69	N 2.81

Spectroscopic Data: Tables 10-12

Experiment 2.6: Reaction of $\text{tmpB}=\text{CR}_2$ with 2-methoxy-1,3,2-dioxaphospholane

To 1.60 g (5.1 mmol) $\text{tmpB}=\text{CR}_2$ in 10 ml toluene was added with stirring 0.62 g (5.1 mmol) 2-methoxy-1,3,2-dioxaphospholane in 20 ml toluene over 10 minutes. No obvious changes in color occurred, nor was any warming observed. The solution was stirred for several weeks at room temperature. The ^{11}B -NMR spectrum showed the presence of the starting material ($\delta^{11}\text{B} = 59.0$ ppm, $h_{1/2} = 560$ Hz) in addition to a small amount of a second substance at $\delta^{11}\text{B} = 36.9$ ppm ($h_{1/2} = 450$ Hz, ca. 15%). A ^{31}P -NMR spectrum contained only the signal of the starting material ($\delta^{31}\text{P} = 132$ ppm).

Experiment 2.7: Reaction of $\text{tmpB}=\text{CR}_2$ with 2-fluoro-1,3,2-benzodioxaphospholane

To 1.94 g (6.2 mmol) $\text{tmpB}=\text{CR}_2$ in 10 ml toluene was added with rapid stirring a solution of 2-fluoro-1,3,2-benzodioxaphospholane in 15 ml toluene over 10 minutes. No apparent reaction occurred. The solution was stirred for 24h, after

which time a ^{11}B -NMR spectrum indicated the presence of starting material at $\delta^{11}\text{B} = 58.4$ ppm. The solution was then refluxed for 2d. 2 signals were then found in the ^{11}B -NMR spectrum: 59.5 and 34.9 ppm, relative intensity = 2.5:1. A ^{31}P -NMR spectrum of the same solution indicated the presence of almost exclusively the starting phospholane ($\delta^{31}\text{P} = 125$ ppm, $J(^{31}\text{P}\text{-}^{19}\text{F}) = 1310$ Hz). The solution was refluxed until no more $\text{tmpB}=\text{CR}_2$ could be detected by NMR (2d), but all attempts at isolating the reaction product by low-temperature crystallization resulted in failure. Only small amounts of the starting material $\text{tmpB}=\text{CR}_2$ were retrieved.

Experiment 2.8: Reaction of $\text{tmpB}=\text{CR}_2$ with 2-chloro-1,3,2-benzodioxarsolane

To 2.00 g (6.4 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added with stirring a suspension of 1.4 g (6.4 mmol) 2-chloro-1,3,2-benzodioxarsolane in 15 ml toluene. After stirring for 3h, a yellow precipitate had formed, which was filtered off, washed with 2 x 5 ml pentane and dried *in vacuo*. The ^{11}B -NMR spectrum of the remaining solution indicated the presence of one boron-containing product at $\delta^{11}\text{B} = 26.7$ ppm ($h_{1/2} = 210$ Hz). Attempts to isolate this or any other product by removing solvent and crystallizing from pentane or hexane failed. The yellow solid isolated from the original reaction mixture contained, according to its ^{11}B -NMR and ^1H -NMR spectra, a mixture of chloro-9-fluorenylidenearsane and 2-(2,2,6,6-tetramethylpiperidino)-1,3,2-benzodioxaborolane. The exact ratio of the two substances could not be determined since much of the solid remained undissolved (presumably oligomeric forms of the fluorenylidene-arsane). Attempts at recrystallizing the isolated solid from CH_2Cl_2 /hexane and toluene/hexane solutions failed to yield a cleaner product.

NMR Data:

$$\delta^{11}\text{B} = 26.7 \text{ (} h_{1/2} = 210 \text{ Hz)}$$

Experiment 2.9: Reaction of $\text{tmpB}=\text{CR}_2$ with 2-fluoro-1,3,2-benzodioxastibolane

To 1.16 g (4.7 mmol) 2-fluoro-1,3,2-benzodioxastibolane suspended in 20 ml toluene was added with stirring a toluene solution of $\text{tmpB}=\text{CR}_2$ (1.47 g, 4.7 mmol) over 10 min. After stirring at RT for 2h, a ^{11}B -NMR spectrum indicated the presence of two products: $\delta^{11}\text{B} = 26.4$ ppm ($h_{1/2} = 170$ Hz) and $\delta^{11}\text{B} = 18.4$ ppm ($h_{1/2} = 90$ Hz), rel. intensities = 10:1. The solution was filtered and a yellow-brown solid was isolated (0.40 g, m.p. $> 200^\circ\text{C}$). As in Experiment 18, the solid was so sparingly soluble in CDCl_3 and C_6D_6 that ^1H - and ^{13}C -NMR spectra could not be obtained. Attempts at bringing the 2-(2,2,6,6-tetramethylpiperidino)-1,3,2-benzodioxaborolane to crystallization in hexane or pentane at lower temperatures (-20°C , -78°C) failed.

NMR Data:

$$\delta^{11}\text{B} = 26.4 \text{ ppm } (h_{1/2} = 170 \text{ Hz})$$

Experiment 2.10: Reaction of $\text{tmpB}=\text{CR}_2$ with 2-chloro-1,3,2-benzodioxastibolane

To a stirred suspension of 1.57 g (5.9 mmol) 2-chloro-1,3,2-benzodioxastibolane in 20 ml toluene was added a solution of $\text{tmpB}=\text{CR}_2$ (1.85 g, 5.9 mmol) in 25 ml toluene over 10 min. After 20 min. stirring, the solution had taken on an orange brown color, and an orange precipitate was visible. After stirring for an additional 1.5h, a ^{11}B -NMR spectrum indicated the presence of a single product at $\delta^{11}\text{B} = 26.8$ ppm ($h_{1/2} = 220$ Hz). The solution was filtered, and all solvent removed *in vacuo*. The resulting brown oil was extracted with several portions of hexane and the solution cooled to -20°C . Further cooling to -78°C could not bring the reaction products to crystallization. The precipitate which had been filtered off was washed with pentane (2 x 10 ml) and dried *in vacuo*. It was soluble in neither C_6D_6 nor CDCl_3 , and thus satisfactory ^1H -

and ^{13}C -NMR spectra could not be obtained.

NMR Data:

$$\delta^{11}\text{B} = 26.8 \text{ (} h_{1/2} = 220 \text{ Hz)}$$

Experiments to Chapter 3

Experiment 3.1: Chloro[9-(trichlorogermyl)fluorenyl](2,2,6,6-tetramethyl-piperidino)borane, 3.1

To 1.74 g (5.5 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added with stirring 0.64 ml (1.2 g, 5.5 mmol) GeCl_4 in 10 ml toluene over 10 minutes. The solution turned lighter in color and, after 1h stirring, a precipitate formed. The solution was filtered after 12h, the precipitate redissolved in an additional 10 ml toluene and all fractions combined and cooled to -20°C for 12h whereby colorless, glass-like crystals separated. The suspension was then cooled to -78°C for 2h and filtered. The crystals were washed with pentane (2 x 5 ml) and dried *in vacuo* to yield 2.20 g 3.1 (75%), m.p. = 200°C , dec.

$\text{C}_{22}\text{H}_{26}\text{BCl}_4\text{GeN}$ (529.67)

calc.	C 49.89	H 4.95	N 2.64
found	C 49.93	H 4.96	N 2.65

Mol.Wt: (MS): 529 (^{74}Ge , ^{35}Cl , ^{11}B , correct isotope pattern)

Spectroscopic Data: Tables 13-15

Experiment 3.2: Chloro[9-(trichlorostannyl)fluorenyl](2,2,6,6-tetramethyl-piperidino)borane, 3.2

To 0.93 g (2.9 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added with stirring a slight excess of SnCl_4 (0.80 g, 3.1 mmol) over 10 minutes. After 12h, the solid which had formed was filtered, and all volatiles were removed *in vacuo* (at 25°C , not warmer !). The residue was then taken up in a minimum amount of toluene (ca. 10 ml) and filtered. The solution was cooled to -20°C for 12h, whereby large, yellow, cube-shaped crystals formed. The solution was further cooled to -78°C for

2h and then filtered. The product was washed with pentane (2 x 10 ml) and dried *in vacuo*. Yield: 1.30 g 3.2 (78%), m.p. = 147°C, dec.

$C_{22}H_{26}BCl_4NSn$ (575.77)

calc.	C 45.89	H 4.55	N 2.43
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found	C 46.09	H 4.61	N 2.40
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Mol. Wt. (MS): 350 (^{11}B , ^{35}Cl ; M-SnCl₃), 100%

435 (^{119}Sn , ^{35}Cl , ^{11}B ; M-tmp), 5%

Spectroscopic Data: Tables 13-15

Experiment 3.2a: Reaction of chloro[9-(trichlorostannyl)fluorenyl]-(2,2,6,6-tetramethylpiperidino)borane, 3.2, with Vaska's complex, $IrCl(CO)(PPh_3)_2$

0.20 g (0.4 mmol) 3.2 was dissolved in 15 ml toluene and added dropwise to a stirred solution of Vaska's complex (0.27 g, 0.4 mmol) in 10 ml toluene. The reaction was stirred for 12h. A ^{11}B -NMR spectrum indicated the presence of one product at $\delta^{11}B = 39.5$ ppm ($h_{1/2} = 470$ Hz) and a ^{119}Sn -NMR spectrum showed the presence of S.M. at $\delta^{119}Sn = -177$ ppm. The Vaska complex did not seem to have gone into solution. Toluene was removed and $CHCl_3$ added, but no change was observed in the positions of the signals following several days' additional stirring. Heating the solution to reflux led merely to decomposition of 3.2 (whose thermal instability was already known, based on earlier attempts at recrystallization from warm toluene) and no change in the ^{119}Sn -NMR spectrum.

Experiment 3.3: Reaction of $tmpB=CR_2$ with Me_2SnCl_2

1.10 g (3.5 mmol) $tmpB=CR_2$ and 0.77 g (3.5 mmol) Me_2SnCl_2 were combined in 25 ml and stirred overnight. After 16h, no reaction was observed by ^{11}B or

^{119}Sn -NMR. The mixture was heated to reflux for 3h, after which time a ^{11}B -NMR spectrum indicated the presence of a new product at $\delta^{11}\text{B} = 36.7$ ppm alongside starting material ($I = 1:1.5$). The ^{119}Sn -NMR showed only the presence of Me_2SnCl_2 . Heating the mixture at reflux for an additional 2d resulted in more of the product at $\delta^{11}\text{B} = 37$ ppm but no change in the ^{119}Sn -NMR spectrum

Experiment 3.4: Reaction of $\text{tmpB}=\text{CR}_2$ with Me_2SnBr_2

1.00 g (3.17 mmol) $\text{tmpB}=\text{CR}_2$ and 0.98 g (3.17 mmol) Me_2SnBr_2 were combined in 25 ml toluene and stirred overnight. No apparent reaction had occurred after 12h (no color change, no initial warming). ^{11}B NMR indicated the presence of starting material, as did ^{119}Sn NMR. Stirring for 2 weeks at room temperature resulted in no changes in the NMR-spectra.

Experiment 3.5: Reaction of $\text{tmpB}=\text{CR}_2$ with Me_3SnCl

0.60 g (1.90 mmol) $\text{tmpB}=\text{CR}_2$ was dissolved in 10 ml CH_2Cl_2 and stirred rapidly as a solution of 0.46 g (1.90 mmol) Me_3SnCl was added over 10 minutes. After stirring the reaction mixture for 3d, ^{11}B - and ^{119}Sn -NMR spectra indicated the presence of starting material only. Heating the mixture to reflux for several hours resulted in hydrolysis/oxidation of $\text{tmpB}=\text{CR}_2$ ($\delta^{11}\text{B} = 36$ ppm) but no change in the ^{119}Sn -NMR spectrum.

Experiment 3.6: $\eta^5\text{-}[(\text{Chloro}(2,2,6,6\text{-tetramethylpiperidino})\text{boryl})\text{fluorenyl})\text{-titanium trichloride, 3.3}$

To 1.73 g (5.5 mmol) $\text{tmpB}=\text{CR}_2$ in 20 ml toluene was added with stirring a solution of 1.05 g (5.5 mmol; excess may be used) TiCl_4 in 10 ml toluene over 10

min. The addition was made slowly and carefully and the flask was cooled with a water bath (15°C) as the reaction is quite rapid and violent. A dark precipitate formed immediately. The reaction mixture was stirred an additional 2h and then filtered. The black-green solid was washed with toluene (2 x 10 ml) and pentane (2 x 10 ml) and dried *in vacuo* for 2h. It was then dissolved in a minimum amount of CH₂Cl₂ and the solution filtered. The resulting solution was cooled to -20°C for 24h and -78°C for 4h, the product was filtered, washed with pentane (2 x 10 ml), and dried *in vacuo* to yield 1.46 g dark green needles of 3.3 as the 1:1 CH₂Cl₂ adduct (45%), m.p. = 200°C, dec.

C₂₃H₂₈BCl₆NTi (589.92)

calc.	C 46.83	H 4.78	N 2.37	Cl 24.04
found	C 46.45	H 5.00	N 2.42	Cl 25.19

Mol. Wt. (MS): 435 (M-2Cl + 2H)

Spectroscopic Data:

$\delta^{13}\text{C}$ (CDCl₃) = 15.0 (C4); 32.4, 33.2 (C7,8); 36.4, 36.6 (C3,5); 57.9, 58.0 (C2,6); 125.6, 129.8, 130.2, 130.9, 131.3, 131.6

Additional spectroscopic data are given in Tables 16-18

Experiment 3.7: η^5 -([Bromo(2,2,6,6-tetramethylpiperidino)boryl]fluorenyl)-titanium tribromide, 3.4

To 1.73 g (5.5 mmol) tmpB=CR₂ in 20 ml toluene was added with stirring a solution of 2.01 g (5.5 mmol) TiBr₄ in 10 ml toluene over 10 min. The addition was made slowly and carefully. A dark precipitate formed almost immediately and the solution was stirred an additional 2h and filtered. The black-green solid was washed with toluene (2 x 10 ml) and dried *in vacuo* for several hours. It was then dissolved in a minimum amount of CH₂Cl₂ and the solution filtered and cooled to -20°C for 12h. After cooling to -78°C for 2h, the solution was filtered and the product washed with pentane (2 x 5 ml) and dried *in vacuo* to yield 1.77 g of dark-green needles of 3.4 as the 1:1 CH₂Cl₂ adduct (42%), m.p. > 200°C, dec.

$C_{23}H_{28}BCl_6NTi$ (767.72)

calc.	C 35.98	H 3.68	N 1.82
found	C 36.64	H 4.07	N 1.87

Mol. Wt. (MS): 394 (M-TiBr₃)

Spectroscopic Data: Tables 16-17

Experiment 3.8: η^5 -([Chloro(2,2,6,6-tetramethylpiperidino)boryl]-fluorenyl)(dimethylamino)titanium dichloride, 3.5

To 1.86 g (5.9 mmol) $t\text{mpB}=\text{CR}_2$ in 50 ml toluene was added with stirring 1.19 g (6.0 mmol) $(\text{Me}_2\text{N})\text{TiCl}_3$ as a solid. The reaction mixture was stirred for 2d at 25°C, filtered, and the product washed with pentane and dried *in vacuo* to yield 2.00 g (63%) of green 3.5. 3.5 was insoluble in toluene, hexane, and pentane, but appeared "soluble" in both CH_2Cl_2 and CHCl_3 , yielding in both cases dark green solutions. The product was dissolved in 50 ml CH_2Cl_2 and the solution cooled to -20°C for 12h and to -78°C for an additional 2h and filtered. The product was washed with pentane (2 x 5 ml) and dried *in vacuo* to yield 1.23 g dark green needle-shaped crystals. Characterization by m.p. and ^{11}B - and ^1H -NMR indicated the CH_2Cl_2 adduct of 3.3.

NMR Data (CDCl_3):

$\delta^{11}\text{B} = 38.1$ ppm ($h_{1/2} = 540$ Hz)

$\delta^1\text{H} = 0.93(\text{s}), 1.65\text{-}1.89(\text{m})$ (18H, *tmp*);
7.20.7.78(m, 8H, fluorenyl)

-NMe₂ no longer present

Experiment 3.9: (9-fluorenyl)(isopropoxy)(2,2,6,6-tetramethylpiperidino)borane,

3.7

To 2.00 g (6.3 mmol) $\text{tmpB}=\text{CR}_2$ in 10 ml toluene was added with stirring 1.79 g (6.3 mmol) $\text{Ti}(\text{O}^i\text{Pr})_4$ in 10 ml toluene. The solution became much lighter in color, and the flask became noticeably warm. After stirring for 6h, the ^{11}B -NMR spectrum indicated the presence of a new product at $\delta^{11}\text{B} = 33.0$ ppm. Solvent was removed *in vacuo* and replaced with 20 ml hexane. The resulting solution* was cooled to -20°C for 12h and -78°C for an additional 2h and filtered to yield 1.20 g 3.7 (46%), m.p. = 150°C , dec.

$\text{C}_{28}\text{H}_{40}\text{BNO}$ (417.45)

calc.	C 80.56	H 9.66	N 3.36
found	C 79.50	H 9.06	N 3.62

NMR Data (CDCl_3):

$\delta^{11}\text{B} = 31.5$ ($h_{1/2} = 330$ Hz)

$\delta^1\text{H} = 0.31$ (d, 6H, $(\underline{\text{CH}_3})_2\text{CH-O-}$);

1.48(s, 12H, tmp); 1.72(s, 6H, tmp);

2.57(m, 1H, $-\text{O}-\underline{\text{CH}}(\text{CH}_3)_2$); 4.34 (broad, 1H, C9-H);

7.20(m), 7.59(m), 7.81(m) (8H, fluorenyl)

$\delta^{13}\text{C} = 15.1$ (C4); 33.2 (C7,8); 36.7 (C3,5); 53.2 (C2,6);

23.9 [$(\underline{\text{CH}_3})_2\text{CH-O-}$]; 65.1 ($-\text{O}-\underline{\text{CH-}}$);

120.0 (C14); 124.3 (C11); 125.5 (C12);

126.4 (C13); 141.2 (C15); 147.6 (C10)

* Distillation of the remaining solution yielded only traces (*ca.* 15 mg) of $\text{Ti}(\text{O}^i\text{Pr})_4$ (by ^1H -NMR and C-, H-analyses).

Experiment 3.10: Reaction of $\text{tmpB}=\text{CR}_2$ with hafnium tetrachloride

To 0.84 g (2.6 mmol) $\text{tmpB}=\text{CR}_2$ in 15 ml toluene was added with stirring a suspension of 0.86 g (2.6 mmol) HfCl_4 in 15 ml toluene. The reaction mixture was

stirred for 12h, but no change in color or homogeneity of the solution was observed. A ^{11}B -NMR spectrum indicated the presence of the starting material $\text{tmpB}=\text{CR}_2$ ($\delta^{11}\text{B} = 59.0$ ppm). The toluene was removed and replaced with Et_2O , and the resulting solution (still largely heterogeneous) heated to reflux. After several hours, signals at $\delta^{11}\text{B} = 59, 43$, and 36 ppm (rel. intensities: 4:2:1) were observed. Further refluxing for 3d resulted in complete conversion to two products at $\delta^{11}\text{B} = 42$ and 36 ppm (rel. intensities: 2:1). Filtration of the solution yielded a colorless solid (HfCl_4 , 90%). Attempts to isolate the products from hexane:toluene mixtures (ca. 2:1) at -20°C and at -78°C were unsuccessful.

Experiment 3.11: $\eta^3\text{-}[(\text{Tetrafluoroboronato}(2,2,6,6\text{-tetramethylpiperidino})\text{boryl})\text{-fluorenyl}]\text{rhenium tetracarbonyl}$, 3.9

To 0.32 g (0.8 mmol) $\text{F}_3\text{BFRe}(\text{CO})_5$ suspended in 20 ml CH_2Cl_2 was added with stirring a solution of 0.25 g (0.8 mmol) $\text{tmpB}=\text{CR}_2$ in 5 ml CH_2Cl_2 . The solution turned orange in color upon addition and the suspended rhenium compound began to dissolve. Stirring at RT for 12h resulted in a clear orange-yellow solution which was evaporated to an oil. This was taken up in 2 ml CH_2Cl_2 , filtered and evaporated to an oil which was then triturated with pentane (10 ml) to precipitate a yellow powder which was filtered off, washed with pentane (2 x 5 ml), and dried *in vacuo*. Attempts to obtain single crystals from toluene:hexane mixtures failed. Yield: 0.20 g 3.9 (36%), m.p. = $100\text{-}2^\circ\text{C}$.

$\text{C}_{26}\text{H}_{26}\text{B}_2\text{F}_4\text{O}_4\text{NRe}$ (700.32)

calc.	C 44.59	H 3.74	N 2.00
found	C 43.39	H 4.02	N 1.64

Spectroscopic Data: NMR Data in CDCl_3 , I.R. in CH_2Cl_2

$\delta^{11}\text{B} = 1.1$ ($h_{1/2} = 124$ Hz); -1.0 ($h_{1/2} = 33$ Hz), $I = 1:1$

$\delta^1\text{H} = 1.47(\text{s}), 1.70(\text{m}), 2.16(\text{s})$ (18H, tmp);

$7.24\text{-}7.71(\text{m})$ (8H, fluorenyl)

$\delta^{13}\text{C} = 16.2$ (C4); 27.7 (C7,8); 34.9 (C3,5); 58.1 (C2,6);
119.7; 120.6; 123.9; 124.2; 124.6; 125.3; 125.6;
126.4; 126.9; 127.5; 129.3; 135.0 (fluorenyl);
193.6, 194.1 (CO)

$\nu(\text{I.R.}) = 2050(\text{w}), 2020(\text{vs}), 1950(\text{m}), 1914(\text{vs}) \text{ cm}^{-1}$

Experiments to Chapter 4

Experiment 4.1: Reaction of $\text{tmpB}=\text{CR}_2$ with $\text{CpFe}(\text{CO})_2\text{COCH}_3$ to 4'-(cyclopentadienyl-dicarbonyl-iron)4'-methyl-2'-(2",2",6",6"-tetramethylpiperidino)spiro-[fluorene-9,3'-(1',2'-oxaboretane)], 4.1

To 1.36 g (4.3 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene was added with stirring a solution of 0.95 g (4.3 mmol) FpCOCH_3 in 15 ml toluene over 15 min. The flask became noticeably warm, and the color changed first to light yellow and then to yellow-orange. All volatiles were removed *in vacuo* and the resulting red-brown oil was dissolved in 5 ml toluene and the solution carefully layered with 25 ml hexane. This mixture was cooled to -20°C for 1 week and -78°C for an additional 5h. Filtration yielded yellow-orange crystals which were washed with pentane (2 x 5 ml) and dried *in vacuo* to yield 1.03 g 4.1 (45%), of m.p. = 110°C .

$\text{C}_{31}\text{H}_{34}\text{BFeNO}_3$ (535.28)

calc.	C 69.56	H 6.40	N 2.62
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found	C 71.46	H 6.71	N 2.55
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Mol. Wt. (MS): 535 (^{11}B , ^{56}Fe , 1%)

507 (-CO, 5%); 479 (-2CO, 25%)

358 (-Fp, 100%)

Spectroscopic Data: Tables 21-23

Experiment 4.1a: Thermolysis of 4.1

0.39 g (0.7 mmol) 4.1 was placed in a reaction vessel equipped with a magnetic stir bar and the apparatus evacuated to $9\ \mu$. The flask was then slowly warmed to 120°C , where it was held for 6h. Collecting non-condensable gases with a Toplep pump indicated that no CO- or H_2 -gas was evolved during the course of the

reaction. A red-green crystalline substance was found to have sublimed out of the lower part of the flask leaving behind a brown oily substance. The oil was taken up in CH_2Cl_2 (carefully avoiding the red crystals on the wall of the flask) and a ^{11}B -NMR spectrum indicated the presence of one product at $\delta^{11}\text{B} = 36.7 \text{ ppm}$, $h_{1/2} = 250 \text{ Hz}$. All volatiles were removed *in vacuo* and the resulting oil taken up in hexane (20 ml) and cooled to -20°C . Further reducing the volume of solvent to 10 ml and cooling to -78°C failed to produce a crystalline product. The red-green crystalline product could be identified by m.p., I.R., and ^{13}C -NMR as the dimeric iron complex, $[\text{CpFe}(\text{CO})_2]_2$.

Experiment 4.2: Reaction of $\text{tmpB}=\text{CR}_2$ with $[\text{CpFe}(\text{CO})_2]_2\text{CS}_2$ to $(\text{tmpBC}_{13}\text{H}_8)(\text{CS}_2)$, 4.3

To 1.20 g (3.8 mmol) $\text{tmpB}=\text{CR}_2$ in 15 ml toluene was added with stirring a solution of 1.63 g (3.8 mmol) Fp_2CS_2 in 15 ml toluene. Because of the deep red color of the Fp_2CS_2 solution, it was difficult to observe any obvious color change, though the flask did become slightly warm. After stirring overnight, a ^{11}B -NMR spectrum showed a signal at $\delta^{11}\text{B} = 43.7 \text{ ppm}$ ($h_{1/2} = 250 \text{ Hz}$). Filtration of the reaction mixture yielded 0.94 g of a white powder, which was washed with 2 x 5 ml pentane and dried *in vacuo*. Its ^{11}B -NMR spectrum (CDCl_3) indicated the presence of the boron-containing product at $\delta^{11}\text{B} = 43.3 \text{ ppm}$. The substance was then dissolved in 15 ml CH_2Cl_2 , filtered, and the resulting solution carefully layered with 10 ml of hexane. After cooling to -20°C for several days and to -78°C for an additional 12h, a white crystalline solid was separated and washed with 3 x 5 ml pentane and dried *in vacuo*. Yield: 0.74 g 4.3 (50%) of m.p. 155°C , dec.

$\text{C}_{23}\text{H}_{26}\text{BNS}_2$ (391.40)

calc.	C 70.58	H 6.70	N 3.58	S 16.38
found	C 70.71	H 7.23	N 3.97	S 9.80

Spectroscopic Data: Tables 21-23

The mother liquor was evaporated to dryness and the resulting red-brown solid taken up in 10 ml toluene. This solution was further diluted with 10 ml hexane and cooled to -20°C , whereby a reddish-brown crystalline solid formed and was filtered, washed with pentane (2 x 5 ml) and dried *in vacuo*. It could be characterized as $[\text{CpFe}(\text{CO})_2]_2$ (0.25 g, 37%). ^{13}C -NMR indicated the presence of a small amount (*ca.* 5%) of 4.3, but mostly $[\text{CpFe}(\text{CO})_2]_2$ ($\delta^{13}\text{C} = 88.5$ ppm, Cp).

Experiment 4.3: Reaction of $\text{tmpB}=\text{CR}_2$ with (cyclopentadienyl)bis(triphenylphosphine)ruthenium(phenyl-acetylide)

To 3.48 g (4.4 mmol) $\text{CpRu}(\text{PPh}_3)_2\text{C}\equiv\text{CPh}$ in 20 ml CH_2Cl_2 was added with stirring 1.39 g (4.4 mmol) $\text{tmpB}=\text{CR}_2$ in 10 ml CH_2Cl_2 over 5 min. No apparent reaction occurred. After stirring at 25°C for 2 weeks, a ^{11}B -NMR spectrum indicated the presence of two compounds, the starting material ($\delta^{11}\text{B} = 58.2$ ppm) and a product signal at $\delta^{11}\text{B} = 33.3$ ppm (rel. intensities = 6:1). Heating the mixture to reflux for an additional two days did not affect the relative signal ratios, nor did stirring the mixture at room temperature for 2 more weeks. All attempts to isolate a cycloadduct yielded only the starting material, $\text{tmpB}=\text{CR}_2$.

Experiment 4.4: Reaction of $\text{tmpB}=\text{CR}_2$ with the ethyl ester of acetic acid to 4.5

To 1.13 g (3.6 mmol) $\text{tmpB}=\text{CR}_2$ in 20 ml toluene was added with stirring an excess of $(\text{EtO})\text{COCH}_3$ (0.62 g, 7.0 mmol) in 20 ml toluene. The solution became very warm and noticeably lighter in color. The mixture was stirred for 3h, after which time all volatiles were removed *in vacuo* using a warm water bath (45°C) to yield an off-white solid. This was taken up in 30 ml pentane (30°C) and the resulting solution cooled to -20°C , whereby a white, crystalline solid formed after

12h. The solution was cooled to -78°C for an additional 2h and the solid filtered, washed with 2 x 5 ml pentane and dried *in vacuo*. Yield: 0.95 g 4.5 (65%), m.p. = 109-110°C.

$C_{26}H_{34}BNO_2$ (403.38)

calc.	C 77.42	H 8.50	N 3.47
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found	C 77.02	H 8.86	N 3.50
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Spectroscopic Data: Tables 21-23

Experiment 4.5: Reaction of $tmpB=CR_2$ with N,N-dimethylglycine to N,N-dimethylglycine-[(9-fluorenyl)(2,2,6,6-tetramethylpiperidino)boryl]ester, 4.6

0.97 g (3.1 mmol) $tmpB=CR_2$ was dissolved in 20 ml CH_2Cl_2 and added with stirring to a suspension of 0.32 g (3.1 mmol) N,N-dimethylglycine in 10 ml CH_2Cl_2 over 10 min. at -35°C. The solution was allowed to come to room temperature and was stirred an additional 2h, whereby the solid dissolved. The solvent was then removed *in vacuo* and the resulting red-brown oil was triturated with 40 ml hexane and filtered (leaving N,N-dimethylglycine behind; δ^1H = 3.42, 2.63). The resulting solution was cooled to -20°C for 12h and filtered to yield a slightly yellow solid which was washed with pentane (2 x 5 ml) and dried *in vacuo* to yield 0.67 g 4.6 (52%), m.p. = 72°C.

$C_{26}H_{35}BN_2O_2$ (418.26)

Spectroscopic Data: Tables 21-23

Experiment 4.6: Reaction of $tmpB=CR_2$ with benzoyl chloride to [9-(benzoyl)-fluorenyl](chloro)(2,2,6,6-tetramethylpiperidino)borane, 4.7

To 0.92 g (2.9 mmol) $tmpB=CR_2$ in 15 ml toluene was added with stirring an

excess of benzoyl chloride (0.82 g, 5.8 mmol) in 15 ml toluene over 15 minutes. The solution turned wine-red upon addition and the flask became noticeably warm. The mixture was stirred for 24h after which time a ^{11}B -NMR spectrum indicated complete reaction to a new product at $\delta^{11}\text{B} = 27.3$ ppm ($h_{1/2} = 330$ Hz). All volatiles were removed *in vacuo* at 35°C. The resulting white solid was dissolved in a minimum amount of toluene (ca. 5 ml) and 3 portions of pentane were added. The solution was cooled to -20°C for 12h and to -78°C for an additional 2h and filtered to yield a white crystalline solid, which was washed with pentane (2 x 10 ml) and dried *in vacuo*. Yield: 0.85 g 4.7 (66%), m.p. = 145°C.

$\text{C}_{28}\text{H}_{31}\text{BCINO}$ (443.83)

calc. C 75.78 H 7.04 N 3.16

found C 75.50 H 7.31 N 3.09

NMR Data: Tables 21-23

$\nu(\text{I.R.})$ (Nujol/Hastaflon) = 1670 cm^{-1} (C=O)

Experiment 4.7: Reaction of $\text{tmpB}=\text{CR}_2$ with acetyl chloride to [9-(acetyl)-fluorenyl]chloro(2,2,6,6-tetramethylpiperidino)borane, 4.8

To 0.80 g (2.5 mmol) $\text{tmpB}=\text{CR}_2$ in 15 ml toluene was added with stirring an excess (0.47 g, 6.0 mmol) of CH_3COCl in 15 ml toluene over 10 minutes. The solution immediately turned lighter in color and the flask became slightly warm. The solution was stirred at room temperature for 5d at which time a ^{11}B -NMR spectrum indicated the presence of a product at $\delta^{11}\text{B} = 42.4$ ppm ($h_{1/2} = 350$ Hz) with a shoulder at $\delta^{11}\text{B} = 36.7$ ppm (by extrapolation, the relative intensities were approximately 5:1). All volatiles were removed *in vacuo* and the resulting yellow-brown oil was taken up in 5 ml toluene and 15 ml pentane were added. Attempts at obtaining a crystalline product by cooling the solution to -20°C and then to -78°C were unsuccessful.

Experiment 4.8: (9-Fluorenyl)(methyl)(2,2,6,6-tetramethylpiperidino)borane, 4.10

1.40 g (4.4 mmol) $\text{tmpB}=\text{CR}_2$ and 0.92 g (4.4 mmol) $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ were combined in 50 ml hexane with stirring and heated to reflux for 1h, whereby large amounts of a gas evolved (CH_4), and the solution turned reddish-purple in color. The mixture was cooled to room temperature and a ^{11}B -NMR spectrum indicated the presence of one product at $\delta^{11}\text{B} = 50.6$ ppm ($h_{1/2} = 253$ Hz). The solution was filtered, hexane removed *in vacuo* and replaced with 20 ml pentane. The resulting mixture was filtered, pentane was removed *in vacuo* and then replaced with 20 ml fresh pentane. The solution was stirred for 20 min. at room temperature, filtered, and cooled to -20°C for 12h and to -78°C for 3h, whereby a colorless crystalline solid formed. The solid was filtered quickly, and carefully washed with pentane (2 x 2 ml), and dried *in vacuo*. Yield: 0.30 g 4.10 (21%). Recrystallization from pentane failed to yield a product that with satisfactory analyses, although the ^{11}B -, ^{13}C - and ^1H -NMR spectra were extremely clean (purity > 99%). m.p. = $147\text{-}149^\circ\text{C}$.

$\text{C}_{23}\text{H}_{30}\text{BN}$ (331.31)

NMR Data:

$\delta^{11}\text{B} = 49.5$ ($h_{1/2} = 450$ Hz)

$\delta^1\text{H} = 0.04(\text{s}, 3\text{H}, \underline{\text{CH}_3}\text{-B})$; $1.47(\text{s}, \text{broad})$, $1.65(\text{s})$ (18H, tmp);
 $4.63(\text{s}, \text{broad}, \text{C9-}\underline{\text{H}})$; $7.03\text{-}7.46(\text{m}, 4\text{H})$, $7.56\text{-}7.66(\text{m}, 2\text{H})$,
 $7.79\text{-}8.04(\text{m}, 2\text{H})$ (fluorenyl)

$\delta^{13}\text{C} = 14.9$ (C4); 34.3 (C7,8); 36.6 (C3,5); 55.0 (C2,6);
 33.1 (broad, $\text{H}_3\underline{\text{C}}\text{-B}$); 50.2 (C9);
 120.4 (C14); 124.7 (C11); 126.0 (C12);
 126.7 (C13); 142.5 (C15); 149.4 (C10)

Experiments to Chapter 5

Experiment 5.1: η^2 -[(9-Fluorenylidene)(2,2,6,6-tetramethylpiperidino)-borane]-iron-tetracarbonyl, 5.1

1.00 g (3.2 mmol) tmpB=CR₂ and 1.17 g (3.2 mmol) Fe₂(CO)₉ were combined and stirred in 30 ml toluene until the metal carbonyl had dissolved and the solution taken on a dark red-brown color (ca. 16h). All volatiles were then removed *in vacuo*, whereby yellow Fe(CO)₅ was found in the trap (-196°C, characterized by I.R.). The resulting red-brown oil was taken up in a minimum amount of toluene (ca. 3 ml) and layered with 10 ml hexane. Cooling the solution to -20°C for 3 d, and then to -78°C for an additional 6h yielded large, well-formed, light brown prisms which were filtered off, washed with pentane (2 x 2 ml), and dried *in vacuo*. Yield: 0.74 g 5.1 (48%), m.p. = 137°C, dec.

C₂₆H₂₆BFeNO₄ (483.16)

calc.	C 64.63	H 5.42	N 2.90
found	C 63.92	H 5.66	N 3.45

Spectroscopic Data: Tables 26-29

Experiment 5.2a: Reaction of tmpB=CR₂ with η^5 -(cyclopentadienyl)-cobalt-dicarbonyl

To 1.70 g (5.4 mmol) tmpB=CR₂ in 20 ml toluene was added with stirring a solution of 1.50 g (5.4 mmol) CpCo(CO)₂ in 15 ml toluene over 15 min. No apparent reaction occurred and no gas was evolved. After stirring at 25°C for 12h, the ¹¹B-NMR spectrum indicated the presence of starting material only ($\delta^{11}\text{B} = 59$, $h_{1/2} = 700$ Hz). The reaction mixture was then heated to reflux for 6h whereby a small amount of gas was given off (ca. 12 ml, uncorrected burette measurement).

The ^{11}B -NMR spectrum of the solution showed one boron-containing product at $\delta^{11}\text{B} = 36$ ppm. All volatiles were removed and a large amount of $\text{CpCo}(\text{CO})_2$ was found in the trap (-196°C , characterized I.R.). The resulting brown oil was dissolved in hexane (20 ml) and cooled to -20°C . Neither reduction of the solvent volume nor further cooling to -78°C produced a crystalline product.

Experiment 5.2b: Photolysis of η^5 -(cyclopentadienyl)-cobalt-dicarbonyl in the presence of $\text{tmpB}=\text{CR}_2$: η^5 -(Cyclopentadienyl)- η^2 -[(9-fluorenylidene)(2,2,6,6-tetramethylpiperidino)borane]cobalt-carbonyl, 5.2

2.20 g (7.0 mmol) $\text{tmpB}=\text{CR}_2$ and 2.00 g (7.1 mmol) $\text{CpCo}(\text{CO})_2$ were combined in a quartz photolysis apparatus in 50 ml toluene and stirred rapidly under a N_2 -atmosphere. The solution was then irradiated with a Hg-lamp (Original Hanau Q 150) for 12h whereby *ca.* 155 ml gas (uncorrected burette measurement) was evolved. The apparatus was flushed 3 times with N_2 and the lamp turned off. (It was found that, if the lamp was turned off and the solution left to stand under CO atmosphere, CO was taken up very rapidly by the solution.) The solution was transferred to a 100 ml Schlenk flask, and all volatiles were removed *in vacuo*. The resulting red-brown oil was taken up in 2 ml toluene and layered with 20 ml hexane. The solution was cooled to -20°C for 12h and to -78°C for an additional 2h and filtered to yield a red-brown crystalline solid. The product was washed with pentane (2 x 5 ml) and dried *in vacuo*. I.R. indicated the presence of a small amount of $\text{CpCo}(\text{CO})_2$. The solid was then recrystallized from toluene:hexane (10:1, 25 ml), washed with pentane (2 x 5 ml) and dried *in vacuo* to yield 1.51 g 5.2 (51%), m.p.= 115°C , dec.

$\text{C}_{28}\text{H}_{31}\text{BCoNO}$ (467.31)

calc.	C 71.97	H 6.69	N 3.00
found	C 70.27	H 6.83	N 2.98

Spectroscopic Data: Tables 26-29

Experiment 5.3: η^2 -[(9-Fluorenylidene)(2,2,6,6-tetramethylpiperidino)borane]- η^5 -(methylcyclopentadienyl)-manganese-dicarbonyl, 5.3

2.00 g (6.4 mmol) $\text{tmpB}=\text{CR}_2$ and 1.40 g (6.4 mmol) freshly distilled $(\text{MeCp})\text{Mn}(\text{CO})_3$ were combined in a quartz photolysis apparatus as a toluene solution (50 ml) and stirred vigorously under an atmosphere of N_2 . The reaction mixture was irradiated with a Hg-lamp (Original Hanau Q 150) for 12h, whereby 140 ml gas was evolved (uncorrected burette measurement), and the solution turned dark green in color. With the lamp still turned on, the apparatus was flushed three times with N_2 ; the lamp was then turned off. The resulting solution was transferred to a 50 ml Schlenk flask, and all volatiles were removed *in vacuo* to yield a yellow-green oil. The oil was then taken up in 10 ml toluene and layered with 20 ml hexane. The solution was cooled to -20°C for 12h and -78°C for an addition 3h, whereby a yellow microcrystalline solid formed, which was filtered off, washed with pentane (2 x 5 ml), and dried *in vacuo*. Crystals were obtained by recrystallization from toluene at -20°C over 1 week. Yield: 2.10 g 5.3 (65%), m.p. = $131-4^\circ\text{C}$.

$\text{C}_{30}\text{H}_{33}\text{BMnNO}_2$ (505.35)

calc.	C 71.30	H 6.58	N 2.77
found	C 71.09	H 6.85	N 2.68

Spectroscopic Data: Tables 26-29

Experiment 5.4: η^6 -(Benzene)- η^2 -[(9-fluorenylidene)(2,2,6,6-tetramethylpiperidino)borane]chromium-dicarbonyl, 5.4

2.38 g (7.5 mmol) $\text{tmpB}=\text{CR}_2$ and 1.62 g (7.5 mmol) $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ were combined in a quartz photolysis apparatus with 50 ml toluene and stirred

vigorously under an atmosphere of N_2 . The reaction mixture was irradiated with a Hg-lamp (Original Hanau Q 150) for 12h, whereby 170 ml gas was evolved (uncorrected burette measurement) and a light orange powder precipitated out. The reaction vessel was purged 3 times with N_2 and the lamp then turned off. The solution and precipitate were transferred to a 50 ml Schlenk flask and the mixture was filtered. The bright orange solid was washed with toluene (1 x 5 ml) and pentane (3 X 5 ml) and dried *in vacuo* to yield 2.60 g 5.4 (70%), m.p. = 114°C. The product is stable towards air and water, but not very soluble. NMR measurements were carried out using saturated solutions of C_6D_6 . In $CDCl_3$ the compound decomposed inside of 5 min.

$C_{30}H_{32}BCrNO_2$ (501.40)

calc. C 71.87 H 6.43 N 2.79

found C 71.46 H 6.57 N 2.74

Experiment 5.5: Reaction of $tmpB=CR_2$ with bis(triphenylphosphine)-platinum-ethylene

To 0.69 g (2.2 mmol) $tmpB=CR_2$ in 20 ml toluene was added with rapid stirring a suspension of 1.64 g $(PPh_3)_2Pt(C_2H_4)$ (2.2 mmol) in 20 ml toluene. No gas evolution was observed, although the color did slowly turn from orange to yellow-green over 4h. The solution was stirred for 12h at RT, after which time a ^{11}B -NMR spectrum indicated complete reaction to a single product at $\delta^{11}B = 43.5$ ppm ($h_{1/2} = 230$ Hz). Solvent was removed *in vacuo* and replaced with pentane:toluene (ca. 2:1, 20 ml). A small amount of orange solid could be isolated (23 mg), it contained no boron (by ^{11}B -NMR), and its ^{31}P -NMR spectrum indicated largely the presence of one complex at $\delta^{31}P = 51.0$ ppm ($J(^{31}P-^{195}Pt) = 2250$ Hz), which could be assigned to the starting material. Further attempts to obtain a crystalline product from pentane at -20°C were unsuccessful.

Experiment 5.6: Reaction of $\text{tmpB}=\text{CR}_2$ with bis(cyclooctadiene)nickel:

To 1.65 g (6.0 mmol) $\text{Ni}(\text{COD})_2$ in 25 ml toluene was added with stirring a solution of 1.88 g (6.0 mmol) $\text{tmpB}=\text{CR}_2$ in 25 ml toluene over 10 min. No apparent immediate reaction occurred. After stirring for 24h, the ^{11}B -NMR spectrum indicated complete reaction to a single product at $\delta^{11}\text{B} = -43.3$ ppm ($h_{1/2} = 280$ Hz). Attempts to isolate a crystalline product from hexane:toluene (2:1) at -20°C and -78°C were unsuccessful.

X-ray Crystal Structure Determinations¹⁴⁾

The single crystals used for the X-ray crystal structural determinations were transferred under argon atmosphere to a heated-out Lindemann tube and were optically adjusted on a Syntex R3 four-circle diffractometer. The program SHELXTL 80 was used for structural determinations and solutions.

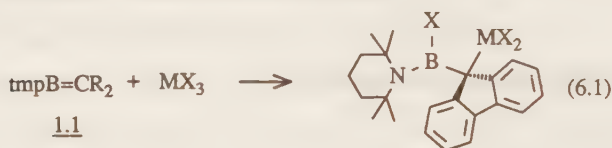
Selected bond lengths and angles are presented in the corresponding Tables along with the discussions of the structures.

Details of the structural solutions as well as complete lists of bond parameters, atomic coordinates and the list of anisotropic temperature factors are available from Prof. Dr. H. Nöth at the Institut für Anorganische Chemie of the University of Munich.

Summary and Conclusion

One of the goals of the present work has been to investigate the reactivity of the first representative of the class of amino-methylene-boranes, the compound (2,2,6,6-tetramethyl-piperidino)(9-fluorenylidene)borane towards Lewis acidic metal halides of Main Groups IV and V. In particular, we were interested in uncovering both steric and electronic effects which influence the reactivity of $\text{tmpB}=\text{CR}_2$ towards such compounds.

In Chapter 1, the general reaction (eq. 6.1)



was shown to lead to stable products for the cases: $\text{M} = \text{P}, \text{As}, \text{Sb}$; $\text{X} = \text{Cl}, \text{Br}$. It was furthermore demonstrated that substitution of the phosphorous atom with one NMe_2 group or with one or two alkyl groups led to the formation of stable products. With increased alkyl substitution and, thus, decreased Lewis acidity, the reactions tended to be slower, but the products (in particular from the reaction between PPh_2Cl and $\text{tmpB}=\text{CR}_2$, compound 1.12) tended to be more stable.

An X-ray crystal structure of the PCl_3 addition product 1.2 was carried out and confirmed the structural suggestion made on the basis of NMR and mass spectral data.

In Chapter 2, the reactivity of $\text{tmpB}=\text{CR}_2$ towards cyclic compounds of P(III) , As(III) , and Sb(III) was investigated. In four cases, compounds of P(III) (2-halogeno-1,3,2-dioxaphospholanes) were found to react to stable products which resulted from the transfer of a halogen rather than an oxygen atom. A bulky phospholane, 2-chloro-1,3,2-tetramethyldioxaphospholane was found to react to a stable addition product, but the reaction required 4 weeks' stirring at room temperature. In Chapter 1 it had been discovered that tmpPCl_2 and $^t\text{BuPCl}_2$ do not react, most likely because of steric reasons. The successful, albeit slow, reaction

with the tetramethylphospholane was interpreted as having taken the kinetically stabilized system $\text{tmpB}=\text{C}_{13}\text{H}_8$ to its steric limits.

In general, it was found, in both Chapters 1 and 2, that the P-F, P-O, and P-N bonds fail to add across the $\text{B}=\text{C}$ double bond. In contrast to this behavior, the cyclic compounds of As(III) and Sb(III) (2-halogeno-1,3,2-dioxametallolanes) reacted to the seven-membered rings which result from the addition of one M-O bond across the $\text{B}=\text{C}$ double bond, and then further to the heterocycle, 2-(tmp)-1,3,2-boroxolane and the corresponding (9-fluorenylidene)(halogeno)-arsananes and -stibanes. The intermediate seven-membered ring could not be observed.

In Chapter 3, the reactivity of $\text{tmpB}=\text{CR}_2$ towards metal halides of germanium and tin was investigated. These reactions led to the formation of stable addition products. Alkyl tin chlorides were also investigated but found not to react, most likely owing to their decreased Lewis acidity (eq. 6.2).



$\text{M} = \text{Ge}, \underline{3.1} \quad n = 0$

$\text{Sn}, \underline{3.2}$

for $\text{M} = \text{Sn}, \text{R} = \text{Me}, n = 2, 3$, no reaction

Reaction of $\text{tmpB}=\text{CR}_2$ with TiX_4 ($\text{X} = \text{Cl}, \text{Br}$) was found to lead to stable addition products. The structure of these products was found, however, to be quite different from the Main Group IV and V addition products. The fluorenyl ligand was found to coordinate in a η^5 -fashion via its central five-membered ring. This could be proven by an X-ray structural determination. It provides one of the rare examples known in the literature in which a fluorenyl ligand is found to form a stable η^5 -transition metal complex and it is the first case for titanium altogether (Fig. 6.1).

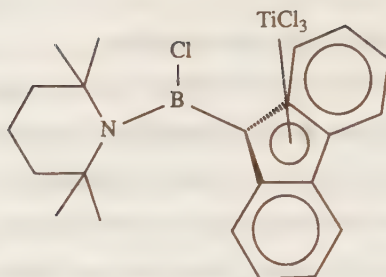
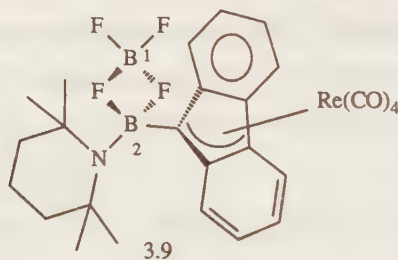


Fig. 6.1

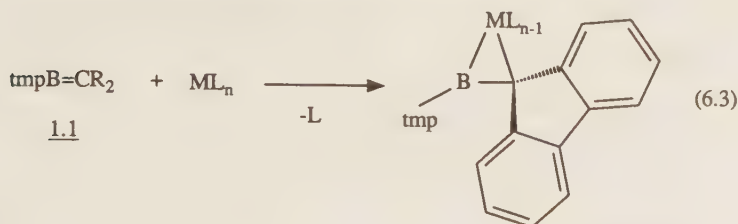
The reaction with the Lewis acidic transition metal cation $\text{Re}(\text{CO})_5\text{BF}_4$ was found to lead to a $\eta^3\text{-Re}(\text{CO})_4$ complex of $\text{tmpB}=\text{CR}_2$, for which the unsymmetrical structure 3.9 was suggested based on spectroscopic data.



In Chapter 4, reactions between $\text{tmpB}=\text{CR}_2$ and variously substituted ketones, esters, thioesters, acid chlorides, and amino acids were investigated. The cycloaddition product from $\text{CpFe}(\text{CO})_2\text{COCH}_3$ and $\text{tmpB}=\text{CR}_2$ was characterized by X-ray crystallography. Acetic acid ethyl ester reacted to give the (2+2) cycloadduct; acid chlorides reacted with transfer of a chlorine atom, though the carbonyl group was found to interact with the B-atom *via* one of the lone pairs on oxygen. The protected amino acid N,N-dimethylamino glycine reacts by transferring a proton to C9 of the fluorenyl ligand followed by irreversible ring closure *via* the NMe_2 moiety forming a bond to the B-atom, resulting in tetracoordination at boron.

In Chapter 5, the reactivity of $\text{tmpB}=\text{CR}_2$ towards transition metal carbonyls and olefin complexes was to be investigated. It was found that metalla-bora-cyclopropanes are formed according to eq. 6.3 for the cases: $\text{ML}_n = \text{Fe}(\text{CO})_4$, $\text{CpCo}(\text{CO})$, $\text{MeCpMn}(\text{CO})_2$, and $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_2$. All reactions

involved the photolytic extrusion of one CO ligand with the exception of the complex with $\text{Fe}(\text{CO})_4$, which was formed from the room temperature reaction with $\text{Fe}_2(\text{CO})_9$ with loss of $\text{Fe}(\text{CO})_5$. X-ray crystal structures of the $\text{Fe}(\text{CO})_4$ and $\text{MeCpMn}(\text{CO})_2$ complexes have been obtained and confirm their structures as bora-olefin complexes. They are the first metallabora-cyclopropanes ever synthesized, and among very few transition metal-boron bonds ever characterized by X-ray crystallography.



Thus, reactions of $\text{tmpB}=\text{CR}_2$ have been shown to be extremely useful in the syntheses of metal halide addition products of Main Groups IV and V; of novel η^5 - and η^3 -boryl-substituted complexes of the fluorenyl ligand; and of the first known and structurally characterized bora-olefin transition metal complexes.

References and Footnotes

(listed according to Chapter)

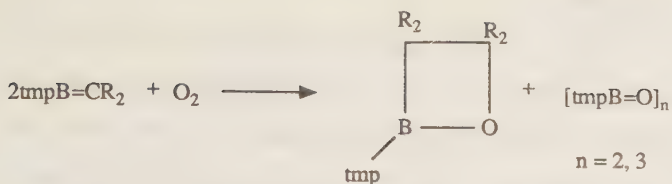
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 $\delta^{13}\text{C} = 13.2$ ($\text{CH}_3\text{-Cp}$)
82.3 (tertiary Cp $\underline{\text{C}}$ -atoms)
102.8 (quaternary Cp $\underline{\text{C}}$ -atom)

- 225.6 (broad, CO)
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